WETTING OF COPPER BY Ni-P BASED BRAZING ALLOYS

PAVOL ŠEBO, PAVOL DUHAJ

Wetting of copper by three kinds of Ni-P based brazing alloys (NiP10, NiCr14P10 and NiNb10P10) was studied. All three alloys wet copper just after melting. Chromium and niobium improve wetting of copper relatively to the Ni-P braze. The interface between copper and brazing alloys in all cases is a solid solution of copper in Ni-P or Ni-Cr-P or Ni--Nb-P, either as a diffusion zone or as a homogeneous layer. Due to the interaction of copper and brazing alloys a Ni_3P phase arises in each braze containing copper in NiP10, chromium in NiCr14P10 and niobium in NiNb10P10, and a Ni based solid solution containing copper in each braze and chromium and niobium in NiCr14P10 and NiNb10P10 brazing alloys, respectively.

ZMÁČANIE MEDI SPÁJKAMI NA BÁZE Ni-P

Článok sa zaoberá štúdiom zmáčania medi spájkami na báze Ni-P (NiP10, NiCr14P10, NiNb10P10). Všetky tri zliatiny zmáčajú meď hneď po roztavení. Chróm a niób zlepšujú zmáčanie medi vzhľadom na spájku Ni-P. Rozhranie medzi meďou a spájkami tvorí vo všetkých prípadoch tuhý roztok medi v Ni-P, resp. Ni-Cr-P, resp. Ni-Nb-P buď ako difúzna zóna, alebo ako homogénna vrstva. V dôsledku interakcie medi a spájok vzniká v každej spájke fáza Ni_3P obsahujúca meď v NiP10, chróm v NiCr14P10 a niób v NiNb10P10 a tuhý roztok na báze niklu s obsahom medi v každej spájke a obsahom chrómu a nióbu v spájke NiCr14P10, resp. NiNb10P10.

1. Introduction

Study of relationships between the structure, properties and methods of production contributes to the development of modern engineering metallic, ceramic and composite materials with improved properties. Production of bigger engineering complexes needs joining of smaller parts from homogeneous as well as heterogeneous materials. Similarly, by combination of various materials one can obtain

RNDr. P. Šebo, CSc., Institute of Materials and Machine Mechanics, Slovak Academy of Sciences, Račianska 75, P.O.Box 95, 830 08 Bratislava 38, Slovakia.

Ing. P. Duhaj, DrSc., Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 842 28 Bratislava, Slovakia.

material with improved or new properties. For example, electrical semiconductor devices require employment of such technologies that give suitable electrical, mechanical, thermal and chemical environment called for proper function of integrated circuits produced on silicon chips. The knowledge of wetting is important in many areas of material preparation such as powder metallurgy, preparation of composite materials, joining of materials and others. Joining of metal with metal, metal with ceramics or ceramics with ceramics brings demand for new fillers and new and simpler methods of joining. This necessitates a deeper study of the properties of the fillers as well as of the joining.

In some cases, it seems useful to use metallic glasses in the form of a foil for joining materials. Such requirements arise also in the case of joining materials protecting contamination of the joint for application in space industry. Using brazing alloy in the form of a foil is suitable for joining of metallic parts of special shapes, e.g. joining of honeycomb material with a perforated face sheet as a part of jet engine [1].

One of the materials used dominantly to join metals is also nickel based brazing alloy containing 10 w.% phosphorus or other additions like chromium or niobium.

The application of Ni-P based brazing alloys can be extended. The aim of this paper is to understand the processes at the application of Ni-P10 brazing alloys in contact with copper: parameters of wetting of copper by brazing alloy and products of interaction of liquid brazing alloy and copper and the influence of additions of chromium and niobium on these processes.

2. Experiment

Brazing alloys NiP10, NiCr14P10 and NiNb10P10 in the form of band 6 mm wide and 0.05 mm thick were prepared by very rapid quenching of a stream of liquid metal [2]. Brazing alloys before inserting in vacuum furnace to measure contact angle were cleaned in acetone using ultrasound. Copper of technical purity in the form of a disc of diameter 15 mm and thickness 2 mm was also cleaned in acetone with ultrasound. Wetting behaviour was studied in the apparatus given in [3]. It consists of vacuum part with graphite furnace where after reaching vacuum $\sim 10^{-3}$ Pa a sample of copper with brazing alloy was inserted. Attaining given temperature was starting point of the time of wetting. A picture of drop of liquid metal was taken at regular time intervals. The contact angles were measured from the magnified pictures of the drops. Wetting was studied at the temperatures 1123 and 1173 K (some at 1273 K) in a vacuum $\sim 10^{-3}$ Pa for the time up to one hour unless overflow of brazing alloy out of the copper substrate became critical.

After solidifying, the drops on the substrate specimens were cut perpendicularly to the substrate plane and metallographically prepared for scanning electron microscope equipped with the X-ray analyser EDAX. The line concentration profile as well as X-ray distribution images of the relevant elements across the interface between copper and brazing alloy was determined.

3. Results and discussion

The equilibrium structure of NiP10 brazing alloy was investigated by the X--ray phase analysis and electron diffraction [2]. It consists of separated grains of solid solution of phosphorus in nickel and eutectics containing mostly the phase Ni_3P and a small amount of solid solution of phosphorus in nickel in the shape of small islands. Maximum solubility of phosphorus in nickel is at the eutectic temperatures only 0.17 w.%. The brazing alloy NiP10 starts to melt according to the phase diagram at the temperature 1153 K.

Wetting of copper substrate by NiP10 brazing alloy starts just after its melting. The time dependence of the wetting angle of copper by NiP10 brazing alloy for the temperatures 1173 and 1273 K is in Fig. 1. From the graph, it can be seen that the brazing alloy wets copper at the temperature 1173 K well and at the temperature 1273 K it wets very well when after about 20 minutes the wetting angle drops below 20°. Both other brazings containing chromium or niobium show even better wetting (Fig. 2, 3). These brazings at the temperature 1123 K and initial brazing at 1273 K show approximately the same values of the contact angle of wetting. From the mentioned, it is clear that both chromium as well as niobium in NiP10 brazing accelerate the wetting of copper. The values of contact angles of wetting Θ and work of adhesion W_A calculated from the relation

$$W_A = \sigma_{LV}(1 + \cos\Theta) \tag{1}$$

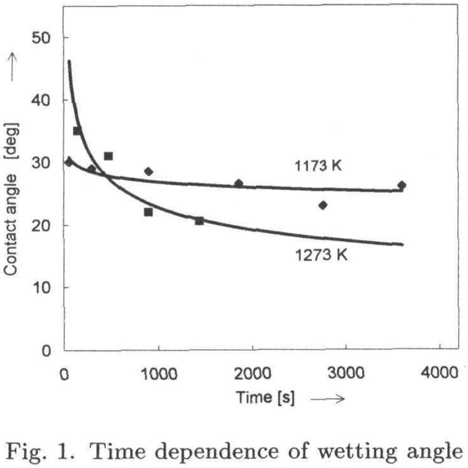


Fig. 1. Time dependence of wetting angle of copper by NiP10 brazing alloy at temperatures 1173 K and 1273 K.

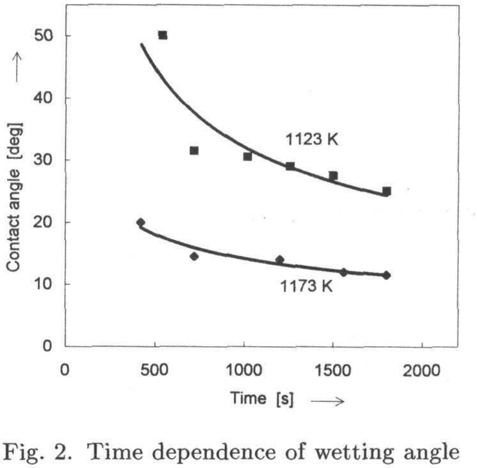


Fig. 2. Time dependence of wetting angle of copper by NiCr14P10 brazing alloy at the temperatures 1123 K and 1173 K.

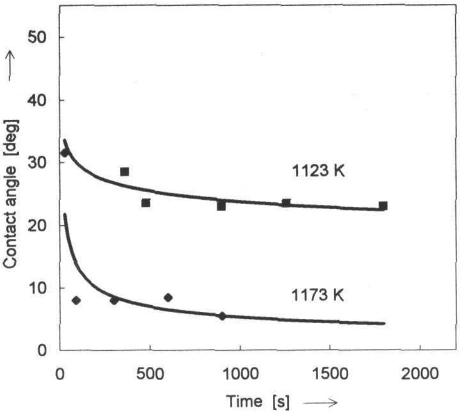


Fig. 3. Time dependence of wetting angle of copper by NiNb10P10 brazing alloy at the temperatures 1123 K and 1173 K.

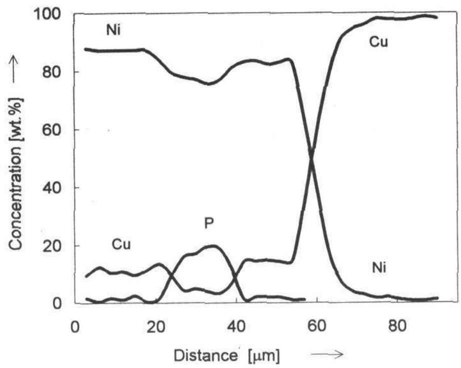


Fig. 4. Concentration profile of Ni, P, Cu across the interface of NiP10 brazing-copper (1173 K, 2 hours).

Table 1. Contact angle of wetting of copper by Ni-P based brazing and work of adhesion. Time of wetting [s] is given in brackets

Material	Contact angle [deg] at the temperature			Work of adhesion [mJ.m^{-2}] at the temperature		
	1123	1173	1273	1123	1173	1273
NiP10		25(3600)	20(1440)		2345	2326
NiCr14P10	24(1800)	12(1800)		2378	2416	
NiNb10P10	23(1800)	8(900)		2385	2428	

are summarized in Table 1.

The surface tension σ_{LV} can be expressed by the relation [4]

$$\sigma_{LV} = 1462 - 0,27T \text{ [K] [mJ.m}^{-2}\text{]}. \quad (2)$$

These values prove high work of adhesion which is a measure of bond strength between brazing alloy and substrate.

From the measurement of concentration profile across the brazing alloy and copper, the following facts result.

At the wetting by NiP10 brazing alloy copper diffuses into brazing. In the interface copper-brazing layer a solid solution of copper in nickel arises and concentration gradient of copper changes from 100 w.% to about 12 w.% and nickel from 85 w.% practically to zero on copper side (Fig. 4). During diffusion of copper at the border, copper-brazing small pores form due to the Kirkendal's effect.

The thickness of the interlayer (the area of the diffusion gradient of copper and nickel) is about 20 μm after two hours of wetting at the temperature 1173 K.

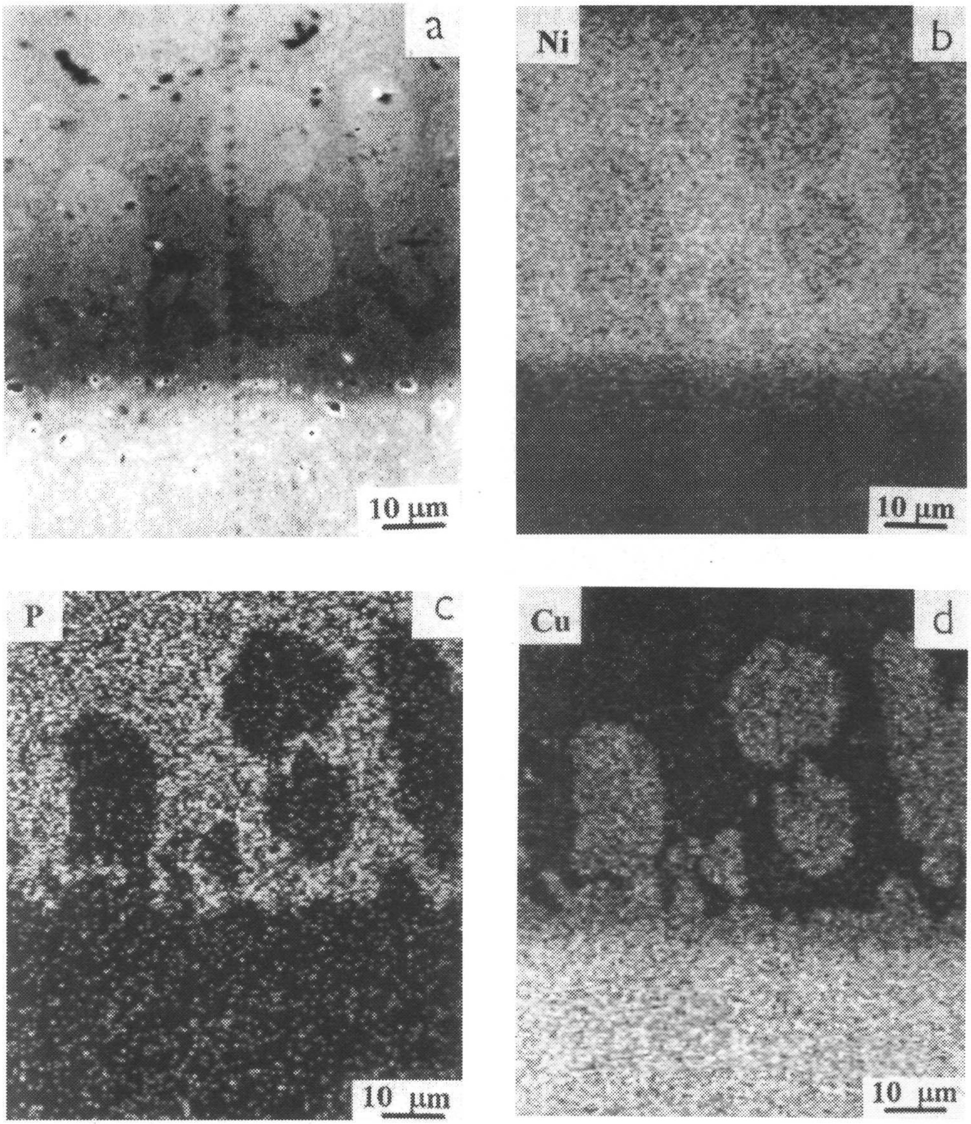
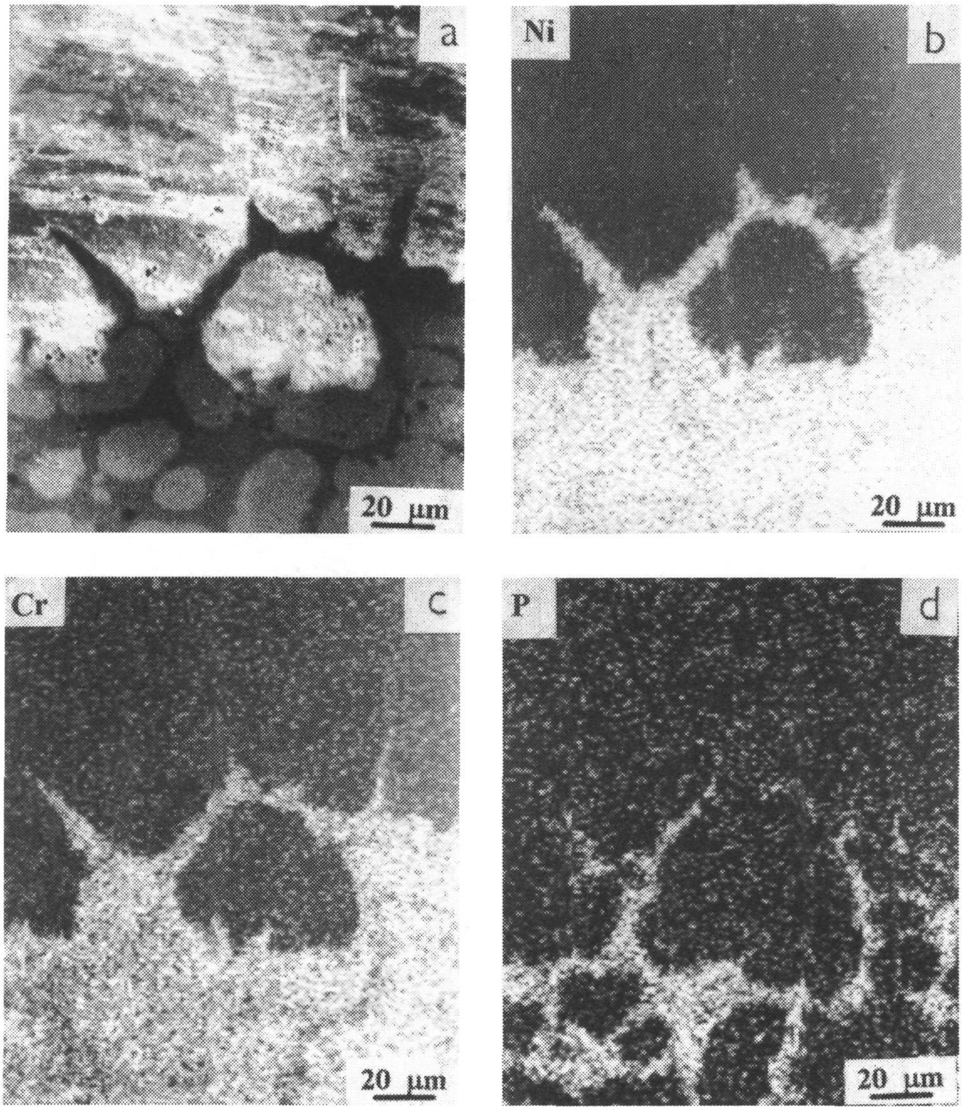


Fig. 5. X-ray distribution image of Ni, P and Cu across the interface of NiP10 brazing--copper (1273 K, 1440 s).

The structure of the brazing metal for these parameters of wetting is composed of a primary nickel based solid solution containing ~ 10 w.% copper and by eutectics with solid solution of the same composition as the primary solid solution and the majority phase $(NiCr)_3P$ with ~ 5 w.% copper.

At the temperature 1273 K after 24 minutes of wetting Cu-Ni solid solution appears again and contains almost 50 w.% nickel and copper and 1 w.% phosphorus. Thickness of this interface for 1273 K and 24 minutes is 6 μm and the copper side



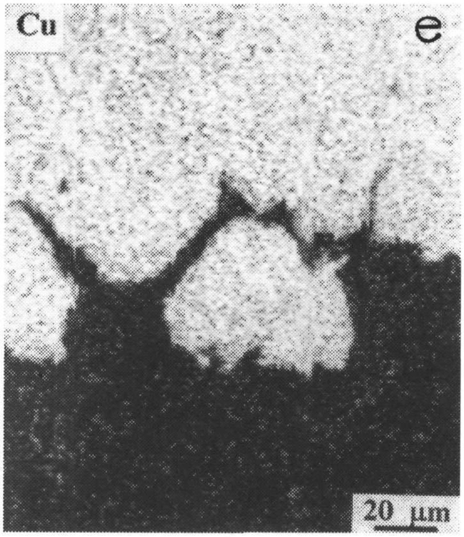


Fig. 6. X-ray distribution image of Ni,Cr,P and Cu across the interface of NiCr14P10 brazing-copper (1123 K, 1500 s).

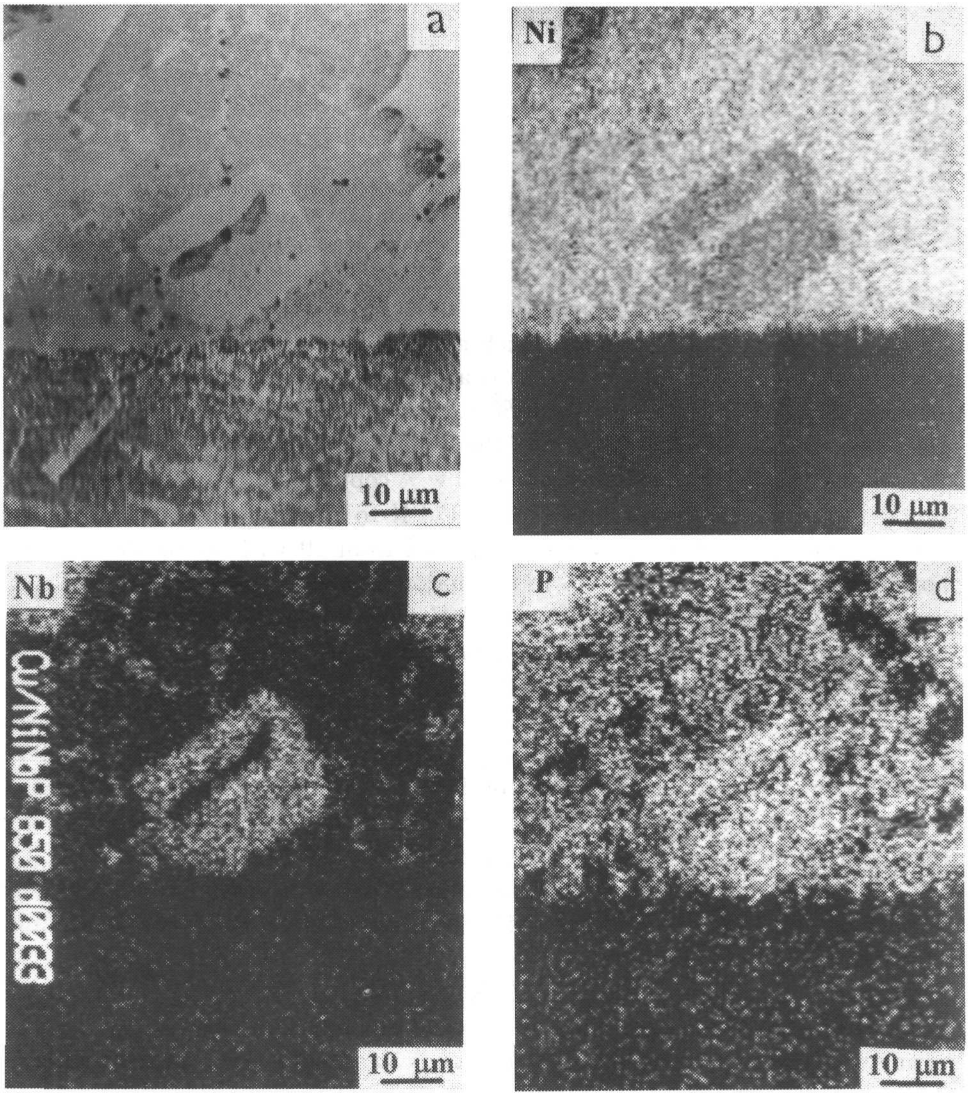
is accompanied by a rise of pores which are due to the Kirkendal's effect. The structure of the brazing metal (Fig. 5) is again constituted by the primary nickel based solid solution containing 49 w.% copper and 1 w.% phosphorus and the eutectics consisting of solid solution of the same composition as the primary solid solution and the $(NiCr)_3P$ phase with $\sim$ 10 w.% copper.

By increasing the temperature from 1173 K to 1273 K, the concentration of copper in the areas of solid solution increased from 10 w.% up to 50 w.% and phosphorus from zero to 100 w.%. In the majority of cases, the eutectic $(NiCr)_3P$ phase content of copper increased from 5 w.% to 10 w.%.

The interlayer at the interface between brazing alloy containing 14 w.% chromium (NiCr14P10) and copper was at the temperature 1123 K very narrow and its composition could not be determined. The brazing containing chromium diffuses at this temperature to copper boundaries and due to this diffusion the interface between copper and brazing becomes broken (Fig. 6). Presence of chromium in brazing slows down diffusion of copper into brazing. The structure of brazing consists of the primary solid solution of nickel containing 20 w.% chromium and 2 w.% copper and the eutectics containing solid solution of the same composition as the primary solid solution and the $(NiCr)_3P$ phase containing 15 w.% chromium and no copper.

At the increased temperature (1173 K) and half hour of wetting, a diffusion of copper into brazing appears. The interlayer at the interface between copper and brazing was again not observed. The brazing is attached to the copper by a sharp boundary in distribution of the present elements. The structure consists of a nickel based solid solution containing 15 w.% copper, 20 w.% chromium and ~ 1w.% phosphorus and eutectics containing solid solution of the same composition and $(NiCrCu)_3P$ phase with ~ 15 w.% chromium and ~ 3 w.% copper. The volume fraction of the $(NiCrCu)_3P$ phase is much smaller comparing to the NiP10 brazing.

The interface between copper and NiNb10P10 brazing is after wetting at the temperature 1123 K for 1440 s composed of diffusion zone containing Ni-Cu solid



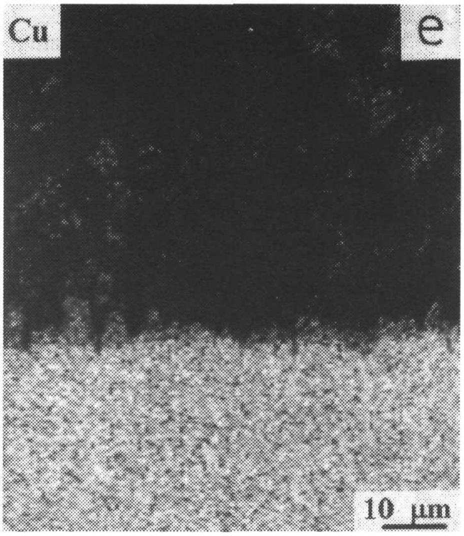


Fig. 7. X-ray distribution image of Ni, Nb, P and Cu across the interface of NiNb10P10 brazing-copper (1123 K, 1440 s).

solution with thickness of ~ 4 mm (Fig. 7). The structure of brazing metal shows that phosphorus content in brazing is higher than that corresponding to the eutectic concentration and due to this fact, by crystallization of brazing, $(NiNb)_3P$ precipitated as a primary phase containing ~ 22 w.% niobium and no copper. The second component of the brazing alloy structure consists of eutectics with a majority of a nickel based solid solution containing 12 w.% copper and ~ 4 w.% niobium and intermediate phase on the base of Ni_3P diluting niobium as well as copper. It can be seen from composition of phases in the case of NiNb10P10 brazing alloy that niobium limits the transport of copper into liquid brazing similarly as it was in the case of brazing containing chromium.

The results obtained by studying the interface between brazing and copper are given in Table 2.

In all three studied brazings, an interlayer composed of solid solution of copper in nickel appears at the interface brazing-copper. Its thickness and composition depend on the parameters of wetting as well as the composition of brazing. With the increase of time and temperature of wetting, the thickness increases and an addition of chromium and niobium in brazing metal lowers concentration of copper in the interlayer. The boundary between the brazing alloy and copper is sharp in the case of NiP10 and NiNb10P10 brazings and is broken in the case of NiCr14P10 brazing. In the first case, (NiP10, NiNb14P10) copper atoms diffuse uniformly through all contact area into nickel or into solid solution of niobium in nickel. In the second case (NiCr14P10) intercrystal erosion of copper substrate arises.

Table 2. Summary of the interaction products of brazings with copper

Brazing alloy	Temperature [K]	Interface	Products of interaction in brazing
NiP10	1173	S.s. Ni-Cu (diffusion zone)	S.s. NiCu10; $(NiCu)_3P$ with ~ 5 w.% Cu
	1273	S.s. (Ni50Cu49P1)	S.s. Ni50Cu49P1; $(NiCu)_3P$ with ~ 10 w.% Cu
NiCr14P10	1123	–	S.s. NiCr20Cu1; $(NiCr)_3P$ with ~ 15 w.% Cr
	1173	–	S.s. NiCr20Cu15P1; $(NiCrCu)_3P$ with ~ 15 w.% Cr and 3 w.% Cu
NiNb10P10	1123	S.s. Ni-Nb-Cu	S.s. NiCu12Nb4; $(NiNb)_3P$ with ~ 22 w.% Nb

S.s. – Solid solution

4. Conclusion

Wetting of copper by NiP10, NiCr14P10 and NiNb10P10 brazing alloys as well as the interaction at the interface between these brazing alloys and copper were studied. The obtained results can be summarized as follows:

1. All these kinds of brazings wet copper just after melting.
2. Addition of chromium and niobium into NiP10 brazing improves wetting of copper.
3. Work of adhesion of all three brazings to the copper is high.
4. Copper at the contact with liquid brazing diffuses into brazing and at the border between brazing and copper a solid solution of copper in nickel or in nickel-chromium and nickel-niobium arises.
5. In all three brazings the brazing joint is composed of two phases. Their fraction, source of origin and composition, depends on the composition of the brazing itself.
6. The primary phase of crystallization of NiP10 and NiCr14P10 brazings is a solid solution based on nickel. The second component of structure of these brazings makes mixture of nickel based solid solution with the composition similar to the primary precipitated phase and intermediary Ni_3P phase in the case of NiCr14P10 brazing containing chromium.
7. The primary phase after crystallization of NiNb10P10 brazing is the $(NiNb)_3P$ phase containing niobium. The second component of the structure consists again of two phase eutectics composed of the $(NiNb)_3P$ phase containing niobium and Ni-Nb-Cu solid solution.
8. Chromium in the brazing NiCr14P10 and niobium in the brazing NiNb10P10 lower the diffusion of copper into the brazing.

Acknowledgements. The present work has been realized in the frame of the grant project GAV 2/1130/95 and international collaboration Copernicus Project CIPA CT 94155. The authors are grateful for partial supporting of this work.

REFERENCES

[1] YEAPLE, F.: Design News, Sept. 1986, 26.
[2] DUHAJ, P.—ŠVEC, P.—MAŤKO, J.—JANIČKOVIČ, D.: Nanostructured Materials, *6*, 1995, 501.
[3] ŠEBO, P.—IVAN, J.—TÁBORSKÝ, L.—HAVALDA, A.: Kov. mater., *11*, 1973, 173.
[4] RHEE, S. K.: J. Amer. Cer. Soc., *53*, 1970, 639.

Rukopis dodaný: 29.9.1995
Rukopis upravený: 22.11.1995