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Co-based brazing fillers

Luty na bazie kobaltu

Abstract

Cobalt-based superalloys are used under high-temperature service conditions. It is often necessary to join parts made of these alloys to construct components with complex geometries. High-temperature brazing is a suitable joining technology. To ensure a good corrosion resistance, the brazing filler and the base material should have similar chemical compositions. This paper deals with the development of near eutectic cobalt-based brazing fillers based on the alloy system Co-ZrC-TaC. The alloys are prepared by arc-melting on a water-cooled copper hearth in an argon atmosphere using a non-consumable tungsten electrode. Geometrical shaping is done by suction casting into a sectioned copper mould. Microstructure and melting behaviour are characterized by means of light microscopy and differential scanning calorimetry.

Streszczenie

Nadstopy na bazie kobaltu są stosowane do pracy w wysokiej temperaturze. Często pojawia się konieczność łączenia elementów wykonanych z tych materiałów w celu uzyskania zaprojektowanej konstrukcji. Lutowanie twarde jest odpowiednią metodą łączenia tych stopów, ponieważ zapewnia dobrą odporność na korozję, przy czym zarówno materiał dodatkowy, jak i materiał lutowany powinny mieć taki sam skład chemiczny. W artykule przedstawiono wyniki prac nad trójskładnikowym lutem przyeutektycznym opracowanym na bazie stopu kobaltu – Co-ZrC-TaC. Stopy wytwarzane są przez topienie łukowe elektrodą wolframową na podkładce miedzianej chłodzonej wodą i w osłonie argonu. Kształt geometryczny nadawany jest w procesie odlewania próżniowego do dzielonej miedzianej formy. Mikrostruktura i zachowanie się topionego metalu analizowano z wykorzystaniem mikroskopii świetlnej i kalorymetrii skaningowej.

Introduction

Co-based materials are widely used in aircraft applications, industrial furnace applications or gas turbine manufacturing. Since the 1960's these alloys play an important role in the fabrication of high-temperature resistant components. The common requirements for the so called Co-superalloys are good high-temperature strength as well as corrosion and creep resistance. The predominant advantage of Co-based materials in comparison to Ni-based superalloys is the higher stability against corrosion in sulphur-containing atmospheres [1]. In order to save material and costs it is preferable to design complex structures consisting of multiple parts. Therefor use of corrosion- and creep resistant brazing fillers is necessary. Nickel-, gold-, or palladium-based fillers are commonly used. In order to lower the melting temperature, the Ni-based materials often contain high amounts of boron, silicon or phosphorous. Especially in case of brazing gaps exceeding a thickness of 50÷80 μm, these elements form brittle intermetallic phases. Because their higher tolerance on gap geometry, the expensive noble metal based fillers are preferred in some industrial processes [2÷3]. Nevertheless especially gold-based fillers show disadvantageous due to erosion effects at the grain boundaries and the local difference in electrochemical potential. To improve the corrosion resistance, the chemical composition of the base material and the brazing filler should be similar. The commercially available Co-based brazing fillers impair the mechanical properties of the basis material induced due to their high liquidus temperatures, causing thermal damage and their poor flow abilities [4÷7]. Because of the requirement of using Ni-free materials inside the human body, the dental industry is one of the exceptions yet.

The aim of this study is the development of new, relatively low melting, good flowing Co-based brazing fillers for use under high-temperature corrosive

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conditions. This is achieved by reducing the melting temperature via addition of hard phase forming refractory metals and carbon. The use of these brazing fillers improve the homogenization of mechanical and corrosive properties within the joints. Additionally, the refractory phases could affect the high-temperature creep resistance positively. For this purpose, the quaternary system Co-Zr-Ta-C shall be modified. The quasiternary cut Co-$ZrC_{0.81}$-$TaC_{0.82}$ is shown in Fig. 1. The first step of the development is the re-evaluation of the experimental data, published by Shurin et al. in the 1990s [8÷9].

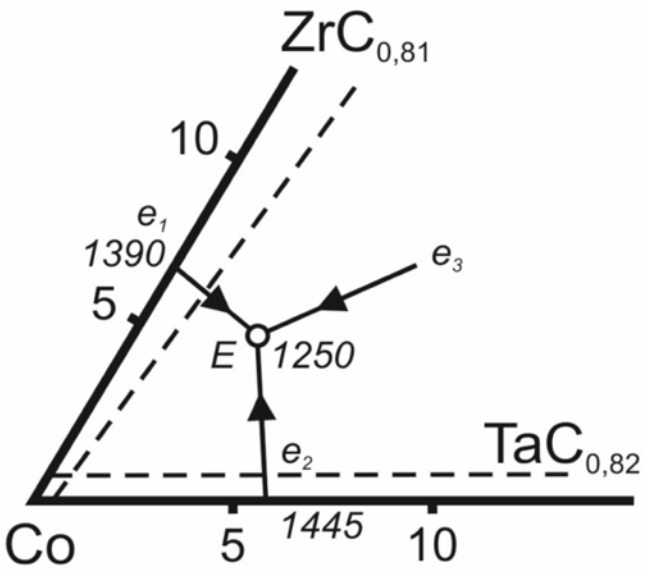

Fig. 1. Quasiternary cut in the quaternary system Co-Zr-Ta-C (axes in at%, temperature in °C)
Rys. 1. Wycinek poczwórnego układu fazowego Co-Zr-Ta-C (osie w % at., temperatura w °C)

Experimental

The alloys were prepared by melting on a water cooled copper crucible in an electric arc furnace using a non consumable tungsten electrode (Fig. 2). The furnace was evacuated to 10^{-2} Pa and refilled with high purity argon (6.0) in order to create a slight overpressure of about $1{,}1 \cdot 10^5$ Pa. Metallic elements with a purity of not less than 99,8 % and spectrally pure graphite were used as starting materials. The compositions of all samples are summarized in Table. The intended weight of the specimens was about 10 g. On the basis of the inert melting procedure, the melting losses can be determined by comparing the charge weight and the resulting alloy weight. Mass losses were measured after each step of alloying using a laboratory scale with an accuracy of 1 mg. After homogenising the samples by continuous flipping over and remelting, suction-casting was carried out in cylindrical moulds that are divided into two sections (Fig. 3).

The specimens were cut into slices by a metallographic cut-off machine using a CBN wheel. In order to ensure a good homogeneity within the samples, X-ray

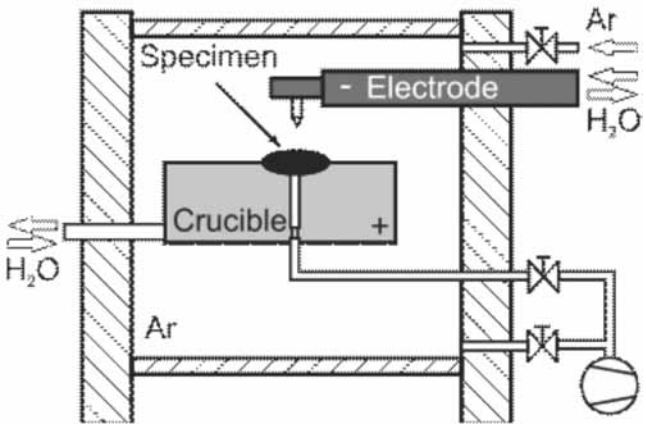

Fig. 2. Schematic drawing of the employed electric arc furnace
Rys. 2. Schemat pieca łukowego

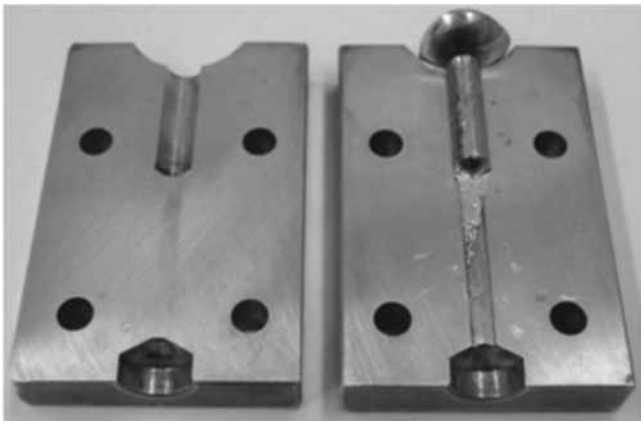

Fig. 3. Cylindrical suction-casting mould
Rys. 3. Cylindryczna forma do odlewania próżniowego

Table. Compositions of the produced samples (balance Co); wt.%
Tablica. Skład chemiczny wytworzonych próbek (reszta Co); % wag..

Sample	Zr	Ta	C	(Zr,Ta)C
1	2.11	2.53	0.36	5
2	2.53	3.04	0.43	6
3	2.95	3.54	0.51	7
5	3.37	4.05	0.58	8
6	3.80	4.55	0.65	9
7	4.22	5.06	0.72	10
8	4.64	5.57	0.80	11
9	5.06	6.07	0.87	12
10	5.48	6.58	0.94	13
11	5.90	7.08	1.01	14
12	6.33	7.59	1.08	15
13	6.75	8.10	1.16	16
14	7.00	8.40	1.20	16.6
15	7.17	8.60	1.23	17
16	7.59	9.11	1.30	18
17	8.01	9.61	1.37	19
18	8.43	10.12	1.45	20

fluorescence analysis (XRF) was carried out at each cut surface. The acceleration voltage was adjusted at 30 keV and a collimator of 2 mm was used to cover a relatively large surface area of the specimen. The measuring procedure can be used to detect elements

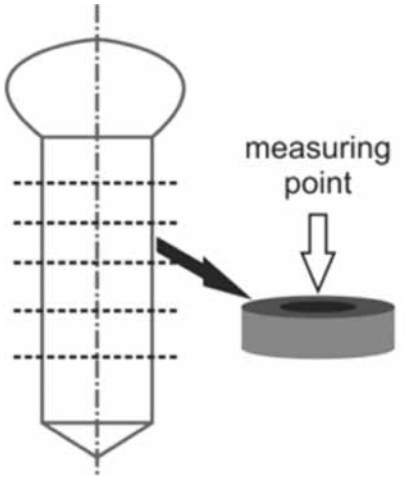

Fig. 4. Position of measuring points in XRF
Rys. 4. Miejsca pomiarów XRF jednorodności odlewu

with atomic numbers above 13, consequently no carbon is detectable. Due to the strong chemical affinity of carbon to the refractory metals and the substoichiometric composition of the carbides $ZrC_{0.81}$ and $TaC_{0.82}$, homogeneity can be ensured by measuring the metal contents. The position of the measuring point on each slice in XRF is shown in Fig. 4.

Parts of the specimens were hot mounted, ground and polished using Struers grinding consumables and polishing cloths. In the last step of preparation, active oxide polishing suspensions were used to obtain a good surface. Microsections were captured by light microscopy using the phase-contrast method.

Differential scanning calorimetry (DSC) was carried out using a NETZSCH STA 449 F1 simultaneous thermal analyzer. The maximum attainable temperature is 1650°C at heating and cooling rates up to 50 K/min. The resolution of the balance is 25 ng at a maximum weight of 5 g. The weighed portion of specimens for DSC is about 50 mg. Because of the high thermodynamic stability of the carbides high heating and cooling rates are need to distinguish the liquidus reaction from base line. The rates were set to 40 K/min.

Results

The total mass losses during the melting procedure did not exceed 0.2 wt%. A good homogeneity was achieved within the specimens. The standard deviation of the XRF measurements did not exceed 2% of the measured value, which is close to the estimated standard deviation of the measuring principle [10]. The results of 20 measurements on the different cut surfaces of one specimen are shown in Fig. 5.

Due to complexity of the alloying system, the evaluation of the DSC curves is difficult. The Co-rich specimens (samples 1÷5) show a tendency to supercooling of the liquidus reaction. The solidus temperature can be determined properly, it decreases almost linearly

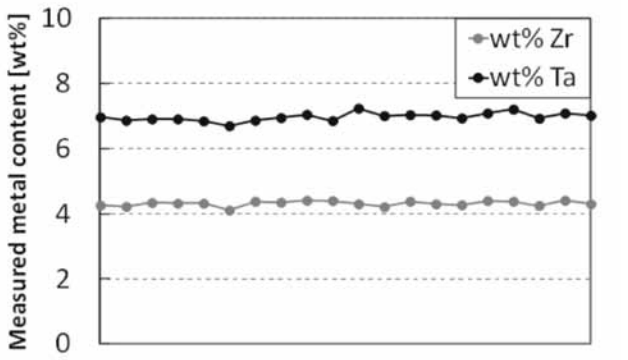

Fig. 5. Metal contents measured by XRF on 20 cut surfaces of one specimen
Rys. 5. Zawartość badanych pierwiastków w 20 odciętych fragmentach próbki (XRF)

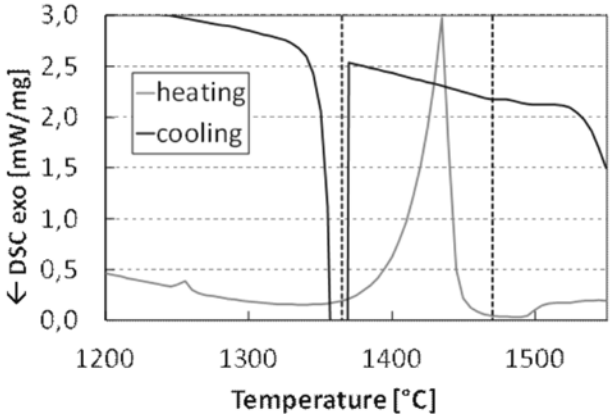

Fig. 6. DSC curve of Sample 10, dashed lines indicate the determined solidus and liquidus temperature
Rys. 6. Krzywe kalorymetryczne dla próbki 10. Linie przerywane określają granicę solidusu i likwidusu

with rising content of alloying elements. Sample 6 is the lowest melting one in the examined range. The determined solidus temperatures (T_{sol}) are constant for samples 7÷10 at a value of 1365°C. Due to the small liquidus reaction and the different possibilities of constructing the onset, the evaluation of the liquidus temperatures (T_{liq}) is ambiguous for hypoeutectic alloys. Therefore the temperatures of the first reaction in the cooling curve and the one of the crystallisation peak were used to determine the melting behaviour of these alloys (Fig. 6). The liquidus temperatures rise almost linearly for samples 7÷10. For higher carbide contents no liquidus reaction can be determined, T_{sol} remains constant at 1365°C.

The melting behaviour of the alloys is strongly dependent on the carbide content. The examined quasibinary cut seems to be eutectic with the lowest melting point at 9 wt% (Zr,Ta)C. The results of the DSC measurements are summarized in Fig. 7.

The micrographs show the dependence of the microstructure on composition of the alloys. Because of the difference in hardness between the relatively soft Co-based matrix and the carbides, the hard phases appear salient. As can be seen in Fig. 8, the dendritic structure disappears induced by the addition of alloying elements. The microstructure of sample 7 (Fig. 8b)

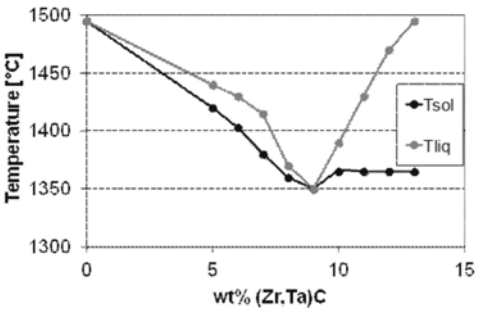

Fig. 7. Determined melting behavior of the alloys in the quasibinary cut Co-(Zr,Ta)C

Rys. 7. Wyznaczone zachowanie się pseudopodwójnego stopu Co-(Zr,Ta)C podczas topienia

is very homogenous with fine dispersed carbides. The further addition of Zr, Ta and C causes the growth of primary carbides, which enlarge with increasing amount of alloying elements. It can be summarised that the micrographs confirm the results of the DSC measurements.

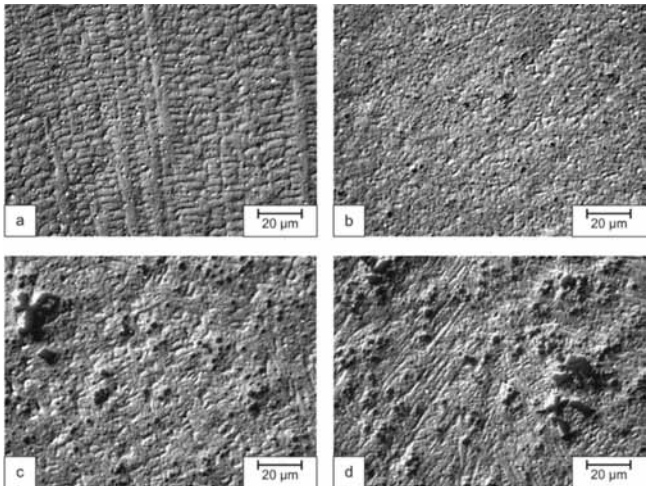

Fig. 8. Micrographs of hypereutectic (a), near eutectic (b) and hypoeutectic (c, d) alloys

Rys. 8. Mikrografie stopu nadeutektycznego (a), przyeutektycznego (b) i podeutektycznego (c, d)

Conclusions

It is possible to melt hard phase reinforced Co-based alloys in an electric arc furnace with very low mass losses (< 0.2 wt%). A good homogeneity can be achieved within the samples using arc-melting and suction-casting techniques. The liquidus temperature (T_{liq}) drops with increasing amounts of alloying elements (samples 1÷6) up to a carbide content of 9 wt% (Zr,Ta)C. It rises with further addition of Zr, Ta and C (samples 7÷10). Due to the specification of the thermal analyzer, T_{liq} is not detectable for carbide contents above 13 wt%. The microstructures of the alloys are in good agreement with the determined melting behaviour. Near the point of the lowest detected melting temperature, the microstructure appears to be very fine dispersed. This indicates a near eutectic composition and confirms the results of the thermal analysis.

The results of Shurin et al. [9] could not be confirmed and should be critically evaluated. The solidus temperature, determined in the present investigation, differs by more than 100 K. The composition of the lowest melting point detected corresponds to about 9 wt% (Zr,Ta)C whilst the literature data published corresponds to about 16.6 wt% (Zr,Ta)C.

References

[1] Davies J. R.: Nickel, cobalt and their alloys. ASM International, 2000.
[2] Greaves W.: Kostengünstige Reparatur von Turbinenschaufeln durch Vakuum-Hartlöten. STR Sulzer Technical Review, 87 (2005) Issue 1, pp.19-21.
[3] Falkenberg S.; Watermeyer K.: Die Untersuchung des Lötverhaltens von auf Ti-Al-Phasen aufgebauten Hochtemperaturwerkstoffen. Sonderbände der Praktischen Metallographie, 27 (1995), pp. 401-404.
[4] Harvey D.: It´s a real gas – for filler metals. Zusatzwerkstoffe für die Fertigung und Reparatur von Gasturbinenkomponenten. Welding and Metal Fabrication, 65 (1997) Issue 10, pp.14-18.
[5] Heikinheimo L.; Miglietti W.; Kipnis J.; Leone E.; Rabinkin A.: Brazing of Co- and Ni-based superalloys using new amorphous brazing filler metals, DVS-Berichte, 212 (2001), pp.30-34.
[6] Donachie M. J.; Donachie S. J.: Superalloys: a technical guide, ASM International.
[7] Greaves W.: Cost effective repairs for IGT vanes. Proceedings of the 3rd IBSC 2006, pp 392-394.
[8] Shurin A. K.; Dmitrieva G. P.; Cherepova T. S.: Phase equilibria in Co-Me′C-Me″C alloys. 1. systems with three-phase eutectic equilibrium, Powder Metallurgy and Metal Ceramics, 35 (1996), Issue 12, pp.615–620.
[9] Shurin A. K.; Dmitrieva G. P.; Cherepova T. S.: Phase Equilibria in Co-Me'C-Me''C alloys. II. Systems with four-phase eutectic equilibrium, Powder Metallurgy and Metal Ceramics, 36 (1997), Issues 3-4, pp.193–196.
[10] Beckhoff B.: Handbook of Practical X-Ray Fluorescence Analysis, Springer Verlag, Berlin (2006).

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