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Ru-Containing Hardmetals: Experimental Studies and Thermodynamic Calculations

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Abstract

WC-Co cemented carbides alloyed with Ru are relevant for the hardmetal industry in spite of their high cost. These alloys are used in applications requiring very demanding thermal properties and good performance in aggressive and abrasive media. For some applications, it is difficult to find an alternative material that could offer a similar performance. Ru containing binders (based on Co, Ni, CoNi and CoNiCr) are analyzed in this work considering carbon contents covering the whole carbon window, and using an equivalent WC-binder Ru-free alloy for comparison. The addition of Ru modifies significantly the chemical composition of the binder which can have important consequences in aspects such as phase formation and grain growth, and also in the final material properties.

Keywords: cemented carbides, Ru-containing binders, Thermodynamic calculations, binder chemistry, hardmetal properties.

Introduction

Co-Ru metallic binders were introduced in the market between 1978-1979, after a period of testing by different hardmetal manufacturers such as Higher Speed Metals Ltd (Sheffield) or Stellram SA (Switzerland) [1-3]. Case studies in the industry demonstrated the superiority of Ru-containing grades, which were claimed to solve some of the most difficult machining problems in the industry. Most notable results were obtained in thread-machining and milling operations, and very significant improvements were obtained when combining CoRu binders with (W, Ta, Nb, Ti)-complex carbides [1-2, 4]. Nowadays most large cemented carbide producers provide Ru-containing grades in their portfolio, and there are plenty of patents covering different uses and compositions. Despite its very high price (currently at about 14 000 € /kg), Ru-containing tools have always maintained their niche of applications.

A large number of patents have been filled, but only a limited number of scientific publications are available. Thus, the reasons for the considerably higher performance of these materials at high temperatures remain being a matter of scientific discussion. There is indeed still very little understanding on the effective mechanisms that enhance the performance of Ru-containing hardmetals, with no clear agreement among different authors. Some of the mechanisms proposed are: a grain refinement effect [5-9], the reinforcement of the WC/WC and WC-Co interfaces [10], a solid solution hardening of the binder phase [5-9][11], or an enhanced FCC to HCP transition [8-9][12][13].

In spite of its importance, almost no studies on Ru-containing hardmetals consider the effect of carbon. Only very recently, some works have considered the analysis of Ru-containing hardmetals at different carbon contents [13] [14][15]. Some works suggest that the transformation from Co (fcc) to Co (hcp) is favored at low carbon contents for slow cooling rates (2-3 °/min), while this tendency is somehow inverted at high cooling rates. [13]. The authors from the patent [14] claim that the processability of these alloys is better, because higher carbon variations are "allowable", i.e. carbon windows are wider.

In a recent publication by Schubert et al. [15] it is shown how the chemistry of the binder phase is significantly altered by the addition of Ru, considerably higher amounts of W being dissolved in Ru-containing binders. This is a very important observation for understanding the effects of Ru in the hardmetal properties because the chemistry of the binder is critical for determining aspects as important as the size and morphology of the WC phase in the microstructure, the intrinsic hardness of the binder phase, or the corrosion resistance of the material. As it is well known, the properties of a hardmetal can differ considerably even within the so-called 2-phase region (region of the phase diagram in which eta carbides and graphite are avoided). The reason is that the W content dissolved in the binder phase (as well as other alloying elements) can be considerably higher at low carbon contents as compared to high carbon alloys.

This paper provides a systematic study of cemented carbides containing WC as the hardphase, combined with 20 wt.% metallic binders with different chemical composition: Co, Ni, CoNi and CoNiCr. This is intended to be a preliminary study to understand whether the trend to increase solubilities in the binder phase, by adding Ru, is reproducible when changing the binder phase composition, and thus to evaluate the potential of Ru for changing the chemical composition of metallic binders with a different nature.

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Experiment

Thermodynamic calculations were carried out for systems containing WC as hardphase, and 20 wt.% of different metallic binder compositions (see Table 1) using the commercially available database TCFE9. Four alloy families were considered: Co, Ni, CoNi and CoNi12wt.%Cr, each of them with and without Ru additions. Ru was added to all binders in an amount of 12.8 wt.%, because this is a Ru content in the range of those typically used in the industry. As Ru is not assessed in the thermodynamic database, calculations are only presented for the alloys without Ru.

Based on the calculations, different gross carbon contents were selected depending on the chemical nature of the binder (see nominal carbon contents of the samples prepared in Table 1). The carbon contents presented in Table 1 were selected to obtain- for each different binder- at least one alloy containing eta carbides, and one alloy presenting graphite. Experimentally, the carbon content was adjusted by adding W powder or graphite to the powder mix. A deagglomerated 3 µm FSSS WC powder was provided by Wolfram Bergbau und Hütten AG (Austria). Standard powder grades were mixed for 2 h in a Turbula mixer without wax. The mixes were pressed at 200 MPa and sintered at 1450 °C for 1 hour in a semi-industrial GCA vacuum sintering furnace on yttria supports to prevent uncontrolled carbon pick up. The cooling rate was about 15-20 °C/min down to 1200 °C.

Sample cross sections were characterized using a Scanning Electron Microscope (SEM) FEI QUANTA 200 ESEM. Energy-Dispersive X-ray Spectrometry (EDS) was used as a semi-quantitative method to identify differences in chemical composition. Binder composition was analysed in coarse binder pools to minimize co-detection of the WC. 5-10 different point analysis were made in the center of large binder pools (~15 µm in diameter) located in the core part of the samples to give average value with a scatter below 1 wt%.

X-Ray diffraction (XRD) was used to identify the phases in stress-free polished alloys, as well as for lattice parameter measurements of the fcc cobalt binder using a PANanalytical X´Pert PRO diffractometer (CuKα1 radiation). For the lattice parameter measurements, the WC peaks were used as an internal standard.

The hardness of the different alloys was determined on cross sections of the samples, following the norm ISO 3878. Indentations were made with a hardness tester M4U 025 by Emco (Austria) applying loads of 30 kgf. No cracks were observed after indentation as 20 wt.% binder was used in these experiments, therefore no evaluation of Palmqvist toughness could be carried out.

Table 1. Composition of the different alloys prepared. All cemented carbides contain 20 wt.% of metallic binder phase, whose compositions are gathered in the table, as well as the name that is used to refer to the alloy thorough the paper.

Binder Alloy (Name)	Binder composition in wt.%	Binder composition in at.%	Nominal C contents (wt.%) in the WC-20wt.%Binder mixes prepared
Co CoRu	100 Co 87.2 Co, **12.8 Ru**	100 Co 92.1 Co, 7.9 Ru	4.48, 4.65, 5.0, 5.2
Ni NiRu	100 Ni 87.2 Ni, **12.8 Ru**	100 Ni 92.1 Ni, 7.9 Ru	4.3, 4.9
CoNi CoNiRu	50 Co, 50 Ni 43.6 Co, 43.6 Ni, **12.8 Ru**	49.9 Co, 50.1 Ni 46.0 Co, 46.2 Ni, 7.9 Ru	4.3, 4.9, 5.2
CoNiCr CoNiCrRu	44 Co, 44 Ni, **12 Cr** 37.6 Co, 37.6 Ni, **12 Cr**, **12.8 Ru**	44 Co, 44 Ni, 13.4 Cr 39.0 Co, 39.2 Ni, 14.1 Cr, 7.7 Ru	4.3, 5.2

Results and discussion

A. Thermodynamic calculations

Fig. 1 shows the isopleths T vs wt.%C of different WC- 20 wt.% binder systems: Co, Ni, CoNi and CoNi12wt.%Cr. The red dashed lines in the diagrams show the nominal carbon contents of the alloys produced experimentally, which should provide at least one sample with eta carbides and one sample with graphite for each binder composition. According to the diagram, 2-phase materials containing only WC and fcc metallic binder should be stabilized at intermediate carbon contents for Co, Ni and CoNi binders. However, in the case of CoNi12wt.%Cr binders, no 2-phase region is observed in the diagram because the amount of Cr added exceeds the maximum solubility in the binder phase, and therefore Cr-rich carbides are stabilized at all carbon contents (M_2C, M_7C_3 or M_3C_2). A more detailed analysis of the chemical composition predicted for the fcc binder phase is presented in Fig. 2, where the composition of the binder phase at different carbon contents is represented for a temperature of 1000 °C. This temperature is chosen because it is the temperature at which the microstructure of hardmetals is generally considered to be “frozen-in”. The red lines represent once again the samples produced in this study. Both at the highest and the lowest carbon contents (i.e. in equilibrium with eta carbides or graphite respectively) the composition of the binder remains almost constant. Within the two phase region, the solubility of W decreases at increasing carbon activities. In contrast, Cr solubility is at maximum in the middle of the carbon window. The reason for this is that Cr is also present in the carbides. In sub-stoichiometric alloys the calculation predicts that Cr is partly dissolved in the eta carbides. At increasing carbon contents, increasing amounts of Cr-rich carbides can be present in the microstructure, which also reduces the amount of Cr effectively present in the binder phase. The amount of Cr dissolved is predicted to be similar in low and in high carbon alloys.

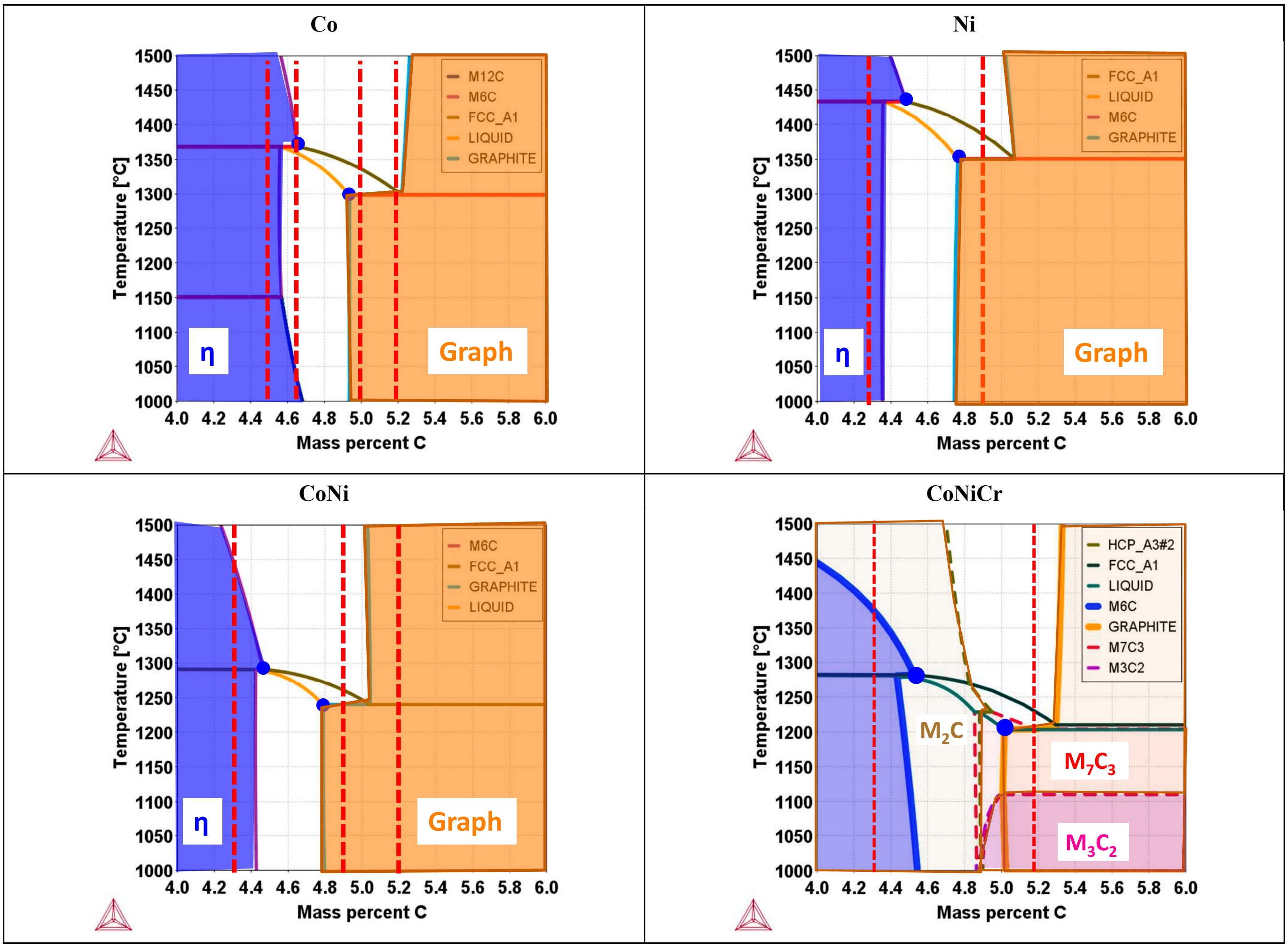


Fig. 1. Isopleths T vs wt.% C of different WC-20 wt.% binder systems. Calculated with the software ThermoCalc using the database TCFE 9. Vertical red dashed lines represent the carbon contents that were prepared experimentally.

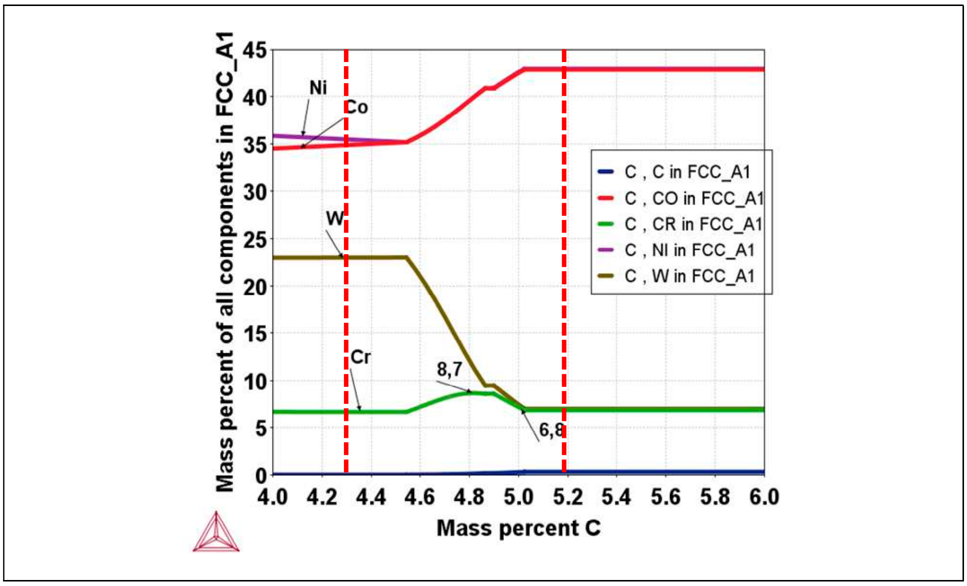


Fig. 2. Evolution of the composition of the binder phase at different carbon contents, for an isothermal temperature of 1000 °C and a binder composition of Co-44 Ni-12 Cr (wt. %)

B. Composition and constitution of the materials prepared experimentally

Sintered materials were characterized in terms of microstructure and chemical composition of the binder phases. The results are summarized in Table 2. All binders (Co, Ni, CoNi and CoNi12Cr) have been analyzed without Ru additions, and with an addition of 12.8 wt.%Ru. In all cases same carbon contents were considered for the two variants (with and without Ru).

As observed in Table 2, all families of alloys presented at least one alloy with eta carbides and one with graphite, which provide, respectively, the maximum and minimum W solubilities in the metallic binder.

The metallic binder only contains XRD diffraction lines corresponding to an hcp phase in the case of Co-based binders. In all other binder families only an fcc phase was detected. In the CoNiCr binders, Cr-rich carbides could be observed in the high carbon variants (see EDS mapping in Fig. 3). The amount of such carbides was rather small, and therefore they could not be detected in the XRD patterns (only after EDS-mapping, or after etching the metallic binder phase with an acidic etchant). In the case of low carbon alloys no Cr-rich carbides could be observed in the microstructure. In these samples Cr is most likely simply divided between the eta carbides and the fcc binder phase.

Table 2. Summary of the composition and constitution of phases observed in the different samples prepared. All materials contain 20 wt% of the indicated binder. The phase composition is described based on the observations from XRD and microstructural examination after selective chemical etching of phases. Compositions are based on EDS point analyses

Alloy family	Nominal C (wt.%)	Phases	Lattice parameter FCC (Å)	W in binder		Cr in binder		HV30
				wt%	at%	wt%	at%	
WC-Co	4.475	WC, fcc, eta	3.577	20.4	7.6			875
	4.65	WC, fcc		19.5	7.2	-	-	870
	5.0	WC, fcc, hcp*	3.558	5.8	1.9	-	-	900
	5.2	WC, fcc, hcp, graph.		3.7	1.2	-	-	-
WC-CoRu	4.475	WC, fcc, eta	3.603	26.3	10.7	-	-	996
	4.65	WC, fcc		25.1	10.1	-	-	945
	5.0	WC, fcc, hcp*	3.591	11.4	4.2	-	-	1000
	5.2	WC, fcc, hcp, graph.		6.4	2.2	-	-	-
WC-Ni	4.3	WC, fcc, eta	3.617	27.9	11.0	-	-	738
	4.9	WC, fcc, graph	3.544	7.7	2.6	-	-	731
WC-NiRu	4.3	WC, fcc, eta	3.617	33.9	14.6	-	-	771
	4.9	WC, fcc, graph	3.576	10.7	3.8	-	-	793
WC-CoNi	4.3	WC, fcc, eta	3.581	25.0	9.6	-	-	833
	4.9	WC, fcc	3.551	6.4	2.1	-	-	785
	5.2	WC, fcc, graph		5.3	1.8	-	-	-
WC-CoNiRu	4.3	WC, fcc, eta	3.613	29.5	12.	-	-	867
	4.9	WC, fcc	3.580	9.4	3.4	-	-	847
	5.2	WC, fcc, graph		8.6	3.1	-	-	-
WC-CoNiCr	4.3	WC, fcc, eta	3.574	19.8	7.3	4.7	6.1	950
	5.2	WC, fcc, Cr-carb, graph	3.547	3.7	1.2	7.9	9.2	805
WC-CoNiCrRu	4.3	WC, fcc, eta	3.610	24.4	9.7	5.1	7.1	1023
	5.2	WC, fcc, Cr-carb, graph	3.583	5.6	1.9	9.0	11.0	876

Samples belonging to the same alloy family were prepared with exactly the same carbon contents for both the variant with Ru and the variant without. Interestingly, the morphology of the eta carbides is different for samples with or without Ru (see Fig. 4). In general, Ru-containing alloys present more dendritic eta carbides (see CoRu, NiRu and CoNiRu alloys in Fig 4), or slightly lower amount of eta carbides as compared with the Ru-free alternative (see CoNiCr and CoNiCrRu alloys in Fig. 4). This is in agreement with the literature suggesting that the carbon window is broadened by the addition of Ru.

This observation is also supported by the W solubilities, which are always increased in the Ru-containing variants. Fig.5 shows the W content in the binder phase of different alloy families, with and without Ru additions. Low carbon variants are represented on the left, and high carbon variants on the right. The low carbon variants (presenting eta carbides) can dissolve significant amounts of W, being at the maximum in Ni binders, and decreasing progressively for CoNi, Co and CoNiCr alloys (the latter ones presenting the minimum values). Exactly the same trend is observed for high carbon variants (containing graphite). Both at the low and at the high carbon variants, the solubility of W in the binder phase is significantly higher in Ru containing alloys. The higher solubilites are also translated in higher lattice parameters for Ru-containing alloys.

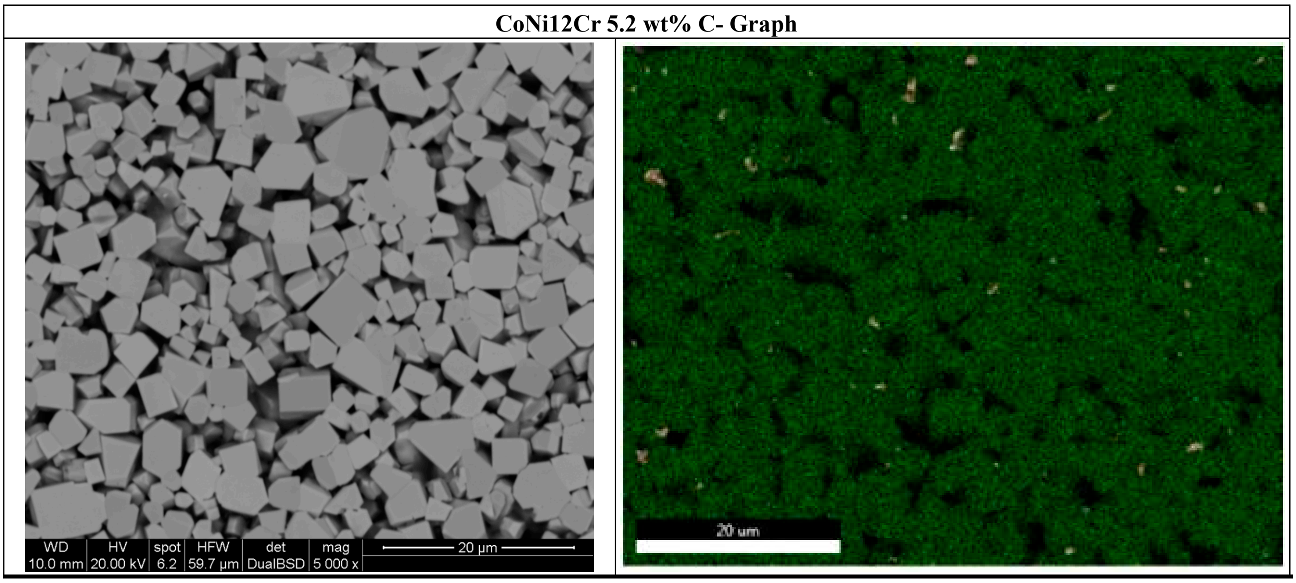
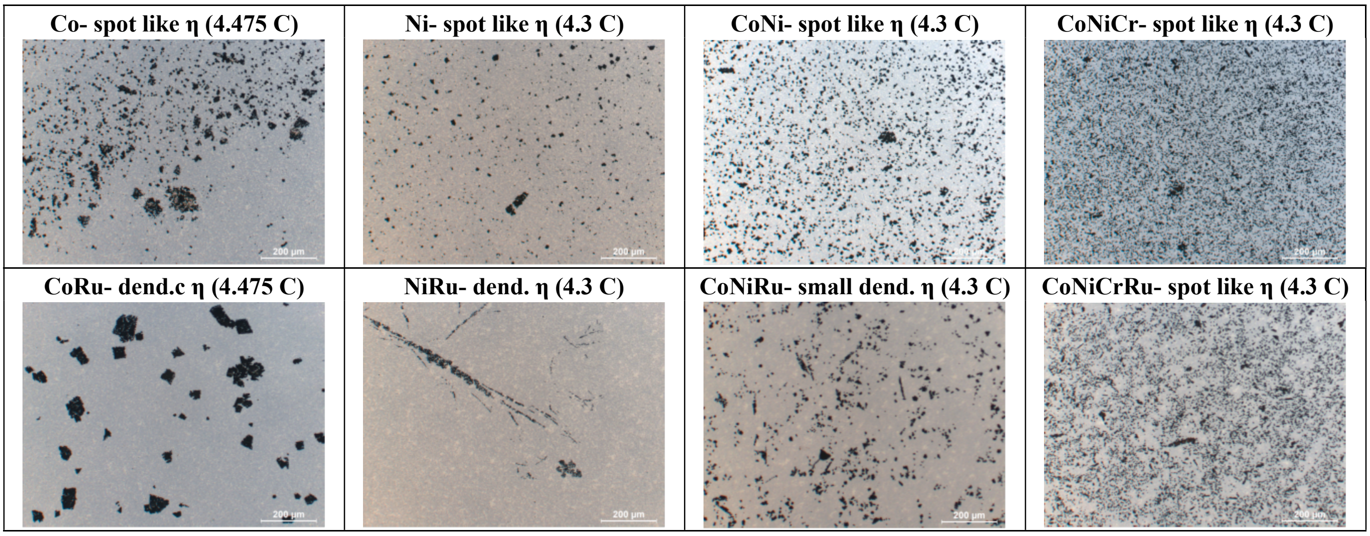

CoNi12Cr 5.2 wt% C- Graph

Fig. 3. Image and EDS mapping of the sample WC-20 wt.% (CoNiCr binder)- 5.2 wt.%C (containing graphite precipitations), after removing the metallic binder phase with Fe3Cl-HCl etchant. Left: Backscattered electrons image, Right; Mapping of elements. W in green and Cr in white. Bright white areas are most likely Cr-rich carbides.


Co- spot like η (4.475 C)

Ni- spot like η (4.3 C)

CoNi- spot like η (4.3 C)

CoNiCr- spot like η (4.3 C)

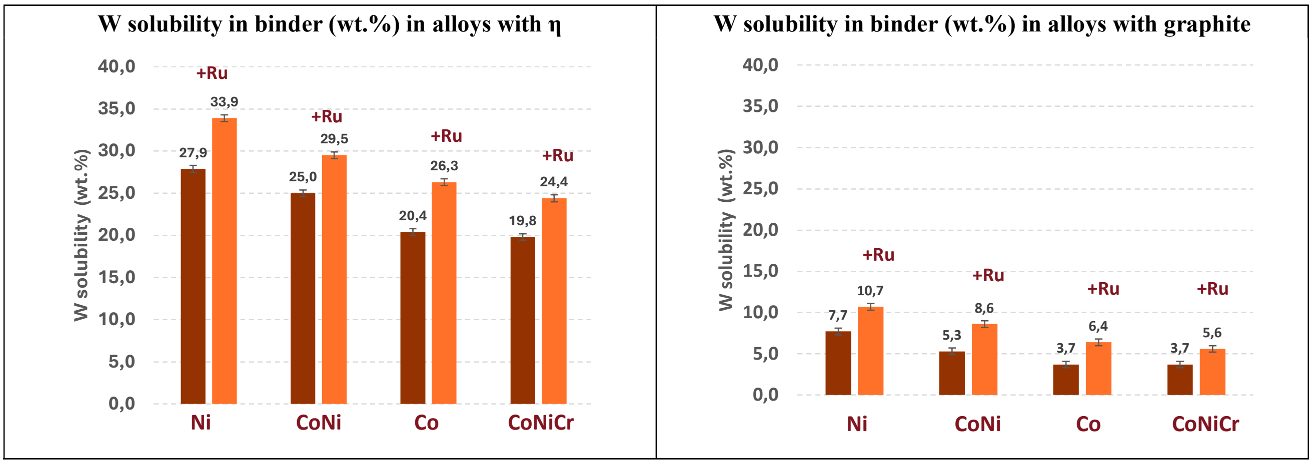
CoRu- dend.c η (4.475 C)

NiRu- dend. η (4.3 C)

CoNiRu- small dend. η (4.3 C)

CoNiCrRu- spot like η (4.3 C)

Fig. 4. Microstructure of samples in equilibrium with eta carbide, after etching 3 seconds with Murakami reagent.


W solubility in binder (wt.%) in alloys with η

W solubility in binder (wt.%) in alloys with graphite

Fig. 5. W solubility in different binder alloys. Left: alloys containing eta carbides. Right: alloys containing graphite. Dark brown bars represent binders without Ru additions (Ni, CoNi, Co, CoNiCr from left to right). Orange bars represent metallic alloys with Ru additions (NiRu, CoNiRu, CoRu, CoNiCrRu from left to right)

The solubility of both Cr and W in CoNiCr and CoNiCrRu alloys are represented in Fig. 6 (left without Ru, right with Ru). The amount of W dissolved in the binder is significantly higher in the low carbon variants. In the case of Cr the differences in solubility between low and high carbon variants are smaller, and the solubility at high carbon contents is even slightly higher than in the low carbon variant (maybe because in the low carbon variant come Cr is dissolved in the eta carbides). Both the solubility of Cr and of W are significantly increased in the Ru-containing materials (represented in the left image of Fig. 6).

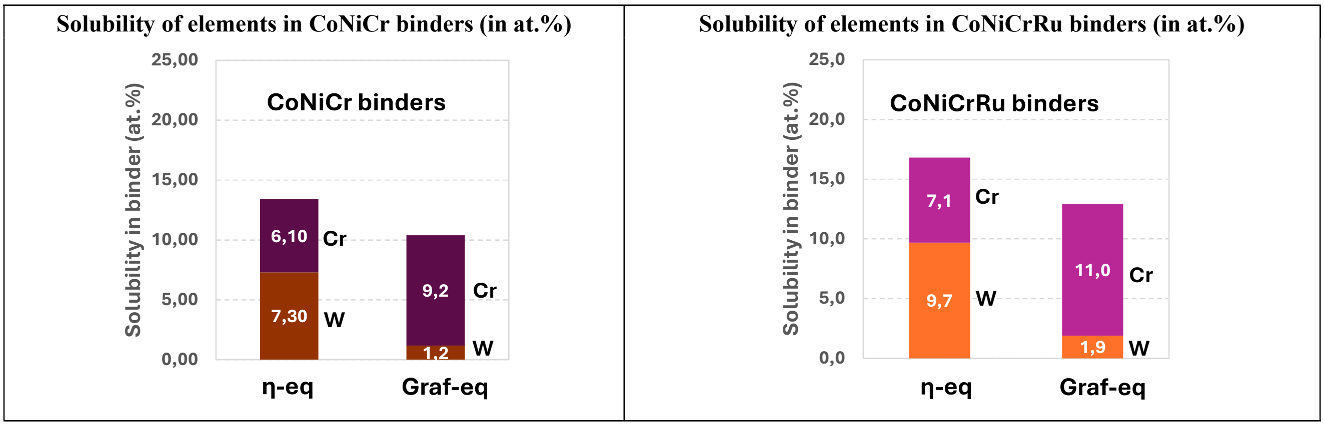


Fig. 6. Solubility of W and Cr in the binder phase, expressed in at. %.. Left: CoNiCr alloys containing either eta carbides or graphite. Right: CoNiCrRu alloys containing either eta carbides or graphite.

When comparing CoNi and CoNiCr binders in Fig. 5, it is clear that, when adding Cr to the binder phase, the solubility of W in the binder is considerably reduced. Therefore, as shown in Fig. 5, the W solubility is lower for CoNiCr families as compared to the other families studied (both with and without Ru additions). However, Cr is in this case dissolved in the binder phase, and this leads to a higher total amount of elements dissolved in the binder, when considering the solubility of both W and Cr. Similar observations have already been reported for Ni-based binders 16). The effect can be clearly observed in Fig. 7, where the total solubility (in at.%) for the elements W and Cr (when applicable), is represented for all alloy families. It is clear from this graph, that the CoNiCr alloys (with or without Ru) present the higher amount of alloying elements dissolved in the binder phase (considering W and Cr as the alloying elements). Also in this case, the total solubility of elements is higher in the low carbon variant and lower in the high carbon, although the difference between low and high carbon is rather small (mainly because of the rather similar Cr solubility in both variants). The results also prove that the addition of Ru not only increases the solubility of W in all binder phases, but it also increases the Cr solubility in both low and high carbon variants.

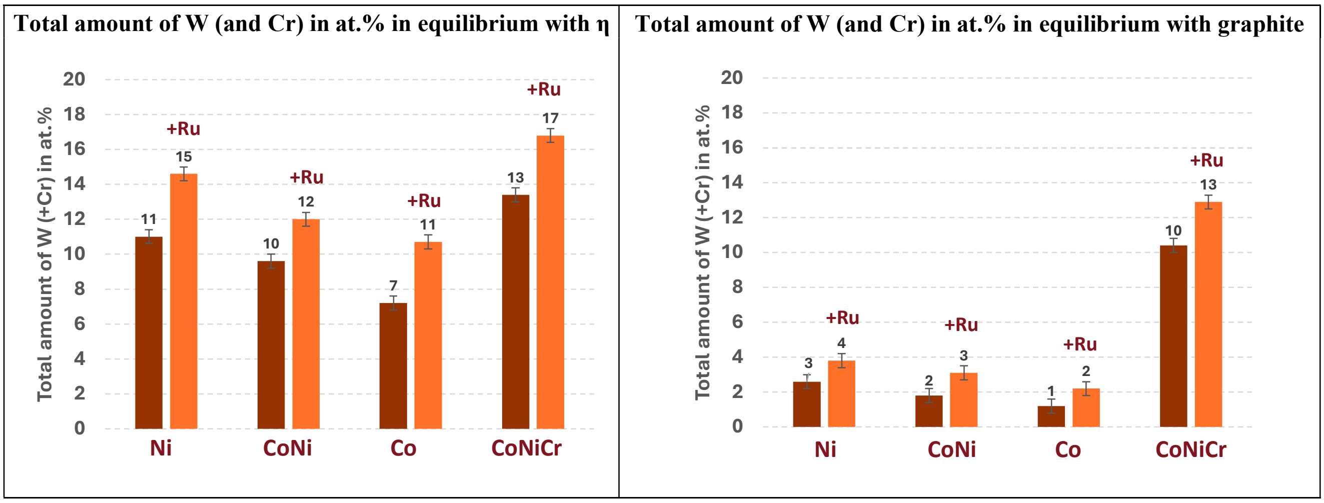


Fig. 7. Total amount of W or W and Cr dissolved in the binder phase, expressed in at. %.. Left: alloys containing eta carbides. Right: alloys containing graphite. Dark brown bars represent binders without Ru additions (Ni, CoNi, Co, CoNiCr from left to right). Orange bars represent metallic alloys with Ru additions (NiRu, CoNiRu, CoRu, CoNiCrRu from left to right)

Conclusions

In spite of its rather high cost, Ru-containing binders are commonly used by the industry for the production of cemented carbides with performance demands at high temperatures. Although many patents have been filled for Ru-containing binders, there is only limited understanding on the mechanisms that affect the higher performance of Ru-containing binders. In a recent study it was shown that the solubility of W in Co-binders is considerably increased by the addition of Ru, both at low and at high carbon contents. This higher solubility of W should not be underestimated, because the W content in the binder can significantly affect properties like e.g. hardness and corrosion resistance 16), and will also have an important effect on the solid solution hardening of the binder phase (solid solution hardening being the only hardening mechanism that can be retained at high temperatures).

This work has extended the study to other binder families, considering Co, Ni, CoNi and CoNiCr binders, both with and without Ru additions. In all binder families, microstructural observations suggest that the carbon window might be increased (at least in the LC region) by the addition of Ru. Besides, the addition of Ru increases the W solubility in all binder families, both at the lowest and at the highest carbon contents (in equilibrium with eta carbides and graphite respectively). The solubility of Cr was also increased by the addition of Ru, at all carbon contents.

In WC-based hardmetals, the addition of Ru in the binder phases (Co, Ni, CoNi) increases the solubility of the elements Cr and W in the metallic binder both at low and high carbon regions. The solubility of W is the lowest in the CoNiCr binder, however, the total amount of elements – Cr and W- dissolved in the binder (considering CoNi as the base) is the highest of all binders.

These preliminary studies on Ru- containing binders with different natures clearly indicate that the presence of Ru can significantly change the chemical nature of the binder, increasing the solubility of elements like W, Cr, and possibly also of C. Further studies are necessary to understand to which extent this change in the binder chemistry can affect aspects such as e.g. grain growth, corrosion behavior as well as intrinsic binder hardness both at low and at high temperatures.

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