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Assessment of fume and chemical hazard in work environment during welding and braze welding of various construction materials by innovative methods

Abstract: It has been presented selected results of investigations oriented on identification, analysis and assessment of fume and chemical hazard which occur during application of innovative methods of joining various construction materials as well as on disclosure of the possibility of optimization of these methods in respect of the improvement in work conditions and the increase in work safety during fabrication of welded structures in different industrial branches. The results of the project "Assessment of fume and chemical hazard in work environment during joining various construction materials by innovative methods as the action supporting the formation of safe work conditions" executed under the Long-term National Programme "Improvement in safety and work conditions" have been given as well.

Keywords: fumes, chemical hazard, welding, weld brazing, work conditions;

Introduction

Occupational safety and health protection are now priorities accompanying the industrial implementation of innovative welding technologies and the improvement of traditional technologies commonly used in the production of welded structures. During welding, braze welding and pressure welding various harmful fume and gas pollutants are emitted to a work environment. Workers are also exposed to physical hazards such as excessive noise, harmful optical radiation and electromagnetic fields. Particularly hazardous for the health of workers are processes in which corrosion resistant steels are welded. Chromium and nickel compounds present in welding fume belong to substances, the carcinogenic effect of which has either been proven or considered highly probable. Recent years have seen the common use of protective coated steels in many industries. Anti-corrosive protective coatings applied as films contain metals and organic substances. Sheets used in the automotive industry are provided with zinc coatings or coatings made of zinc alloys as well as alloys of other metals. Such materials are usually welded, weldbrazed and pressure welded. Joining processes are accompanied by emissions of fumes having a high zinc content or

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chemical compounds belonging to the group of aromatic hydrocarbons. After penetrating the human organism, these substances may cause poisoning or a variety of occupational diseases.

The need to create safe work conditions during industrial welding and allied processes has caused Instytut Spawalnictwa to become involved in the research within the long-term programme "Improving Occupational Safety and Work Conditions" financed and carried out in Poland in the years 2011-2013 within the scope of research and developmental works by the Ministry of Science and Higher Education/National Centre for Research and Development. The Programme Coordinator is the Central Institute for Labour Protection – National Research Institute. Instytut Spawalnictwa is executing an independent project entitled "Assessment of Chemical, Fume and Physical Hazards in the Work Environment Related to Innovative Methods for Joining Various Structural Materials as an Activity Supporting the Assurance of Safe Work Conditions". The first stage of the project was concerned with the assessment of hazards in a work environment during low-energy arc welding and braze welding of corrosion-resistant steels and coated steel sheets [1]. Experimentation in the scope of chemical and fume hazards included the measurements of fume and gas emissions as well as the analysis of the chemical composition of welding fume during CMT (Cold Metal Transfer) and ColdArc welding and braze welding of corrosion-resistant steels and steel sheets provided with anticorrosive protective coatings. The second stage of the project was concerned with hazards in the work environment during resistant welding, friction stir welding and ultrasonic welding and vibration welding of various structural materials [2]. The scope of laboratory tests regarding chemical and fume hazards included tests of the emissions of fumes, gases (CO, NO_x) and organic compounds during spot resistance welding of protective-coated steel sheets, phase identification and the quantitative phase analysis of fumes formed during welding of steel sheets provided with protective coatings.

This article presents the selected results of tests focused on the identification, analysis and assessment of chemical and fume hazards accompanying the use of innovative methods for joining structural materials as well as the optimisation of these technologies in relation to the improvement of work conditions and occupational safety during welding of structures in various industries.

Emissions of fumes and gases and chemical composition of fumes during CMT and ColdArc welding corrosion-resistant steels

Emissions of fume and gas pollutants were tested for CMT and ColdArc gas-shielded arc welding with a limited energy input to a joint. In order to obtain results representative of base metals used presently in various industries it was necessary to carry out tests on two corrosion-resistant steel grades, i.e. austenitic steel X5CrNi18-10 and chromium ferritic steel X6Cr17. Allowing for the necessity to select the type of shielding gas in accordance with production practice and recommendations of electrode wire manufacturers, a welding arc was shielded by gas mixtures characterised by various oxidation rates. The range of shielding gases tested has enabled the assessment of the impact of shielding gas composition on the amount and chemical composition of emitted pollutants. The tests of fume and gas emissions and the analyses of the chemical composition of fumes during welding of stainless steels were carried out for 4 various values of current-voltage parameters, filler wire feeding rates and welding rates. The enumerated technological parameters were selected for all unitary measurements having in view joint (overlay weld) aesthetics, absence of overlay weld reinforcement and the elimination of porosity (elimination of welding imperfections).

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Emission-related (nitrogen and carbon oxides) test results and the results of the analyses of fume chemical compositions enabled a comparative analysis aimed to determine the correlation between the material-technological parameters of the processes and variables. The analyses were concerned with the impact of welding method, current-voltage parameters, shielding gas composition and a base metal type/grade on the (size of) emission of fumes, nitrogen and carbon oxides as well as on contents of various chemical components in fume [1].

Effect of CMT and ColdArc welding of corrosion-resistant steels on the size of pollutant emissions

The tests have revealed that the use of CMT (Cold Metal Transfer) method is connected with significantly lower emissions of fumes, NO_x and CO in comparison with emissions accompanying the use of the ColdArc method [1]. The emission of fume during CMT welding of an X5CrNi18-10 austenitic steel is on the average 30% lower in the whole current range in comparison with ColdArc welding. During welding of an X6Cr17 chromium ferritic steel the emission of fume is lower by 60% (Fig. 1). The size of nitrogen oxide and carbon oxide emissions also depends on a welding method used. CMT is characterised by lower values of NO_x emissions. In comparison with the ColdArc method, the use of the CMT method allows a 25% reduction of nitrogen oxides emission during welding of the austenitic steel and a 35% decrease during welding of the chromium ferritic steel (Fig. 2). The use of the CMT method for welding the austenitic steels reduces the CO emission for the whole window of parameters tested by 40%. In turn, CMT welding of the chromium ferritic steel decreases the emission of carbon oxide by approximately 60% if compared to CO emission levels obtained during ColdArc welding (Fig. 3). The test results have demonstrated that as far as the emission of pollutants into a work environment is concerned, CMT welding of stainless steels is considerably more advantageous. A stable arc, small number of spatters and lower gas and fume emissions make the Cold Metal Transfer method recommendable in terms of the improvement of work conditions during welding sheets made of corrosion-resistant steels.

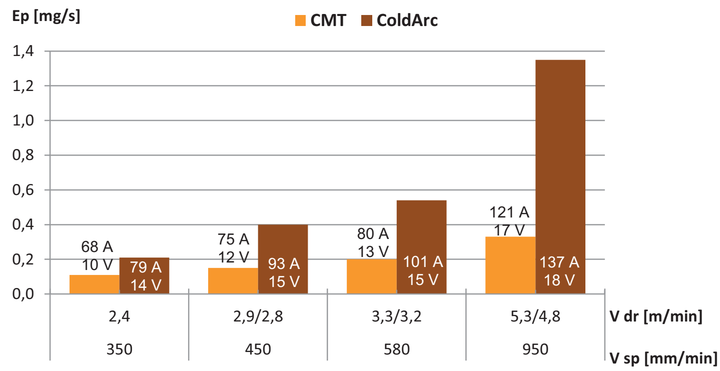

Fig. 1. Fume emission during CMT and ColdArc welding of X6Cr17 chromium ferritic steel using 98%Ar+2%O_2 shielding gas [1]

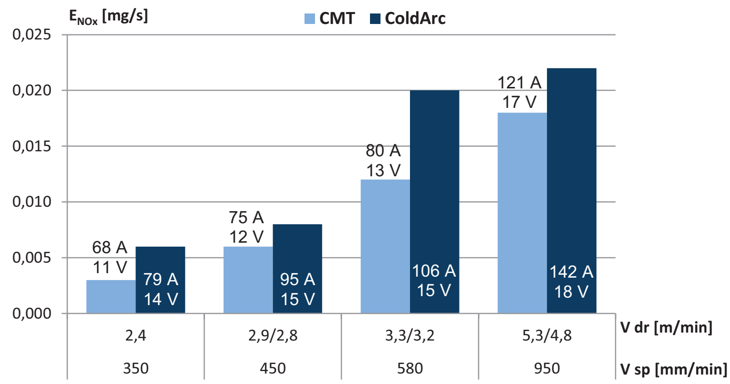

Fig. 2. Emission of nitrogen oxides during CMT and ColdArc welding of X6Cr17 chromium ferritic steel using 98%Ar+2%O_2 shielding gas [1]

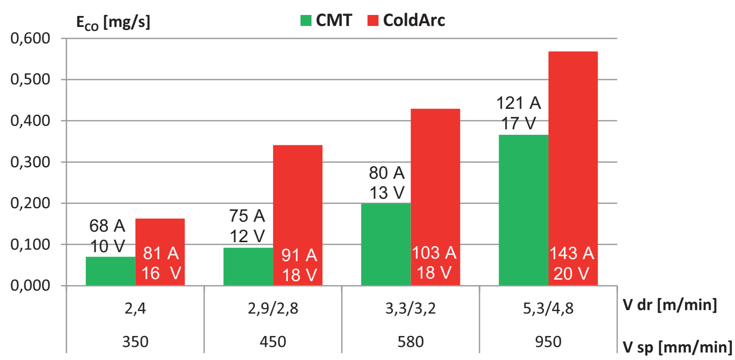

Fig. 3. Emission of carbon oxide during CMT and ColdArc welding of X6Cr17 chromium ferritic steel using 97.5%Ar+2.5%CO_2 shielding gas [1]

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Effect of shielding gas composition on emission of pollutants during CMT and ColdArc welding of corrosion-resistant steels

Testing the size of emissions during welding of the austenitic steel involved the use of argon and two mixtures, i.e. 98% Ar + 2% O_2 and 97.5% Ar + 2.5% CO_2 as shielding gases. In turn, emission-related tests during welding of the chromium ferritic steel involved the use of four gas mixtures varying in oxidation properties. The following shielding gases were used:

- 98% Ar + 2% O_2,
- 97.5% Ar + 2.5% CO_2,
- 82% Ar + 18% CO_2,
- 90% Ar + 5% CO_2 + 5% O_2.

The test results confirmed the existence of a correlation between the size of fume and gas emissions and the type of shielding gas [1,3,4]. During CMT and ColdArc welding of the austenitic steel the highest fume emission accompanied the use of pure argon. During the comparison of the gas mixtures it was observed that a greater fume emission was connected with the use of the mixture 97.5%Ar + 2.5%CO_2. A particularly visible effect of this gas on the size of fume emission accompanied ColdArc welding of the austenitic steel (Fig. 4). Lower fume emission indicators characterised the use of an argon + oxygen (98%Ar+2%O_2) shielding gas.

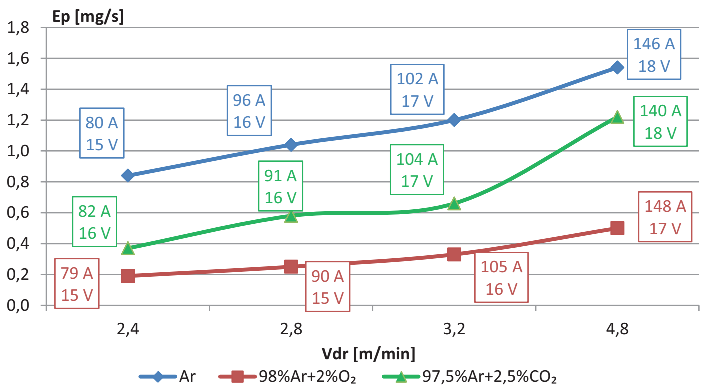

Fig. 4. Effect of shielding gas composition on fume emission during ColdArc welding of austenitic steel [1]

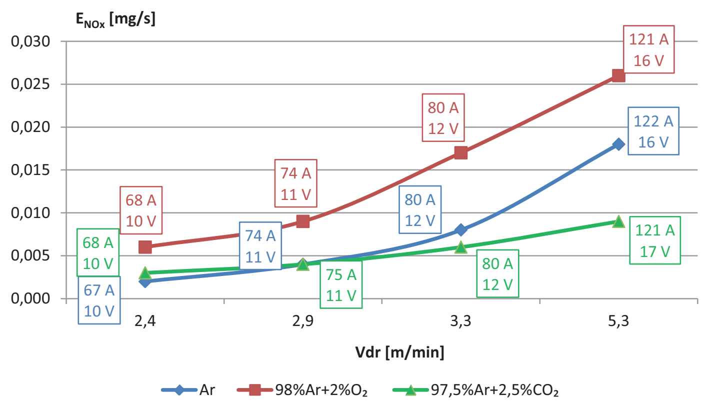

Fig. 5. Effect of shielding gas composition on nitrogen oxide emission during CMT welding of austenitic steel [1]

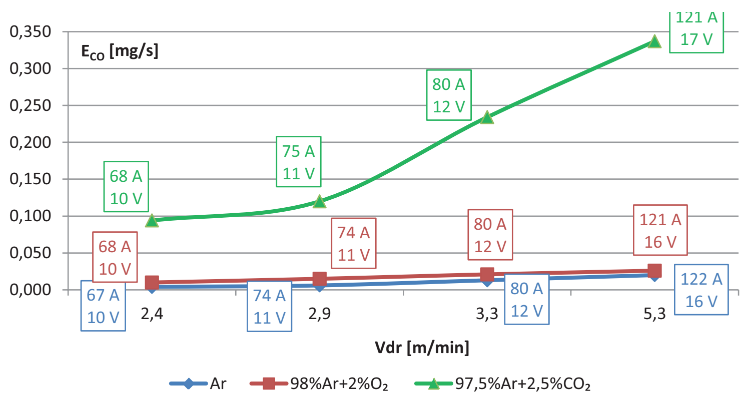

Fig. 6. Effect of shielding gas composition on carbon oxide emission during CMT welding of austenitic steel [1]

During CMT and ColdArc welding of the austenitic steel nitrogen and carbon oxide emissions also depend on the composition of shielding gases. In the whole current range for both welding methods the highest levels of NO_x emission accompanied the use of the 98%Ar+2%O_2 shielding gas mixture. The gas mixture composed of argon + carbon dioxide and pure argon favoured the reduction of nitrogen oxide emission (Fig. 5). The highest carbon oxide emission was connected with the use of the 97.5%Ar+2.5%CO_2 mixture. In turn, the emission of CO to a work environment was reduced when pure argon and the 98%Ar+2%O_2 mixture were used. The aforesaid correlations were determined for both CMT and ColdArc welding methods. An increased carbon oxide emission accompanying the use of the Ar+CO_2 shielding gas mixture can be ascribed to the fact that the main source of carbon oxide during gas-shielded arc welding is the shielding-forming carbon dioxide. As

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a result of the thermal dissociation of CO_2 ($2CO_2 \rightarrow 2CO + O_2$), carbon oxide is emitted to a work environment.

During CMT and ColdArc welding of the chromium ferritic steel the lowest fume emission was observed when the 97.5%Ar+2.5%-CO_2 and 98%Ar+2%O_2 mixtures were used as shielding gases. A significant (2-3 times) increase in fume emission was observed for the 82%Ar+18%CO_2 shielding gas and the 90%Ar+5%CO_2+5%O_2 triple-component shielding gas (Fig. 7). The 82%Ar+18%CO_2 gas mixture reduced the emission of nitrogen oxides; during welding the X6Cr17 steel this mixture was characterised by the lowest NO_x emission indicators (Fig. 8). Due to the necessity of reducing carbon oxide emission during welding the chromium ferritic steel the argon + oxygen mixture is recommended as a shielding gas. The lowest carbon oxide emissions accompanied the use of the 82%Ar+18%-CO_2 shielding gas (Fig. 9).

The tests of fume, nitrogen oxide and carbon oxide emissions during low-energy arc welding of corrosion-resistant steels have revealed the correlation between the type of a shielding gas and the emission of pollutants. In order to reduce fume emissions during welding of austenitic and ferritic steels it is recommendable to use the Ar+O_2 mixture. The highest fume emission was observed for welding of the austenitic steel when pure argon was used as a shielding gas. In turn, the highest fume emission accompanied welding of the chromium ferritic steel when the 82%Ar+18%CO_2 mixture and the 90%Ar+5%CO_2+5%O_2 triple-component mixture were used as shielding gases. In order to reduce nitrogen oxide emissions during welding of corrosion-resistant steels it is advisable to use bi-component Ar+CO_2 gas mixtures. In turn, the reduction of carbon oxide emissions during CMT and ColdArc welding of the austenitic steel requires the use of the Ar+O_2 mixture or pure argon as the shielding gas. The Ar+O_2 mixture can also be used to reduce the emission of carbon oxides during welding of the chromium ferritic steel.

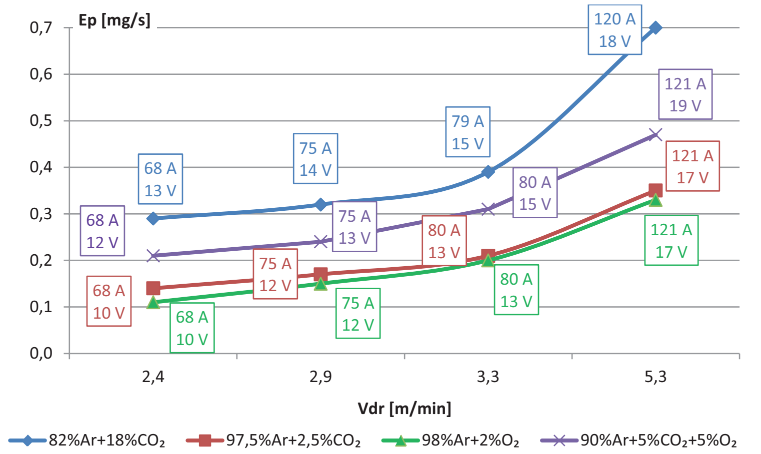

Fig. 7. Effect of shielding gas composition on fume emission during CMT welding of chromium ferritic steel [1]

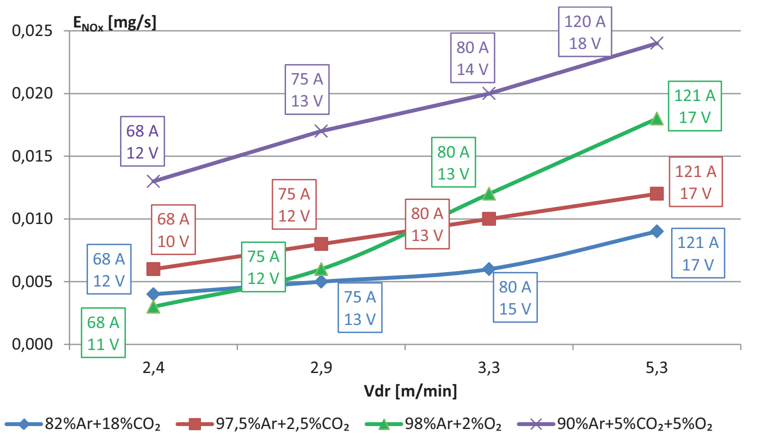

Fig .8. Effect of shielding gas composition on nitrogen oxide emission during CMT welding of X6Cr17 steel [1]

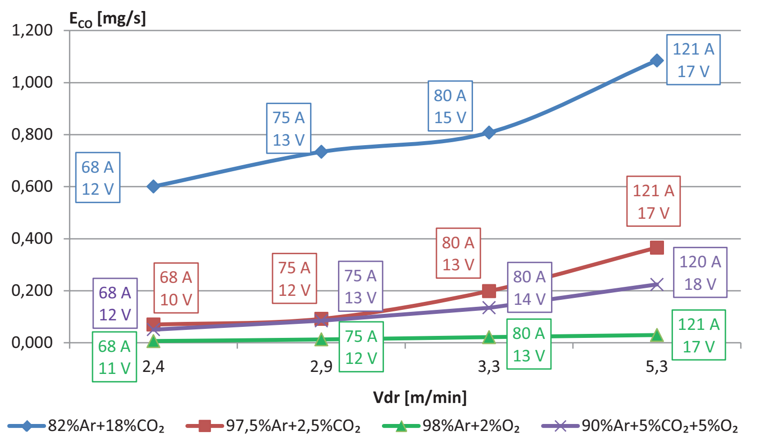

Fig. 9. Effect of shielding gas composition on carbon oxide emission during CMT welding of X6Cr17 steel [1]

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Effect of shielding gas composition on the content of carcinogenic substances in fume during welding of corrosion-resistant steels

While assessing work conditions during welding of corrosion-resistant steels it is necessary to include the effect of shielding gas composition not only on total fume emission but also on the content of chromium(VI) and nickel compounds in the fume. The test results have led to a conclusion that the physicochemical properties of a gaseous shielding have a significant impact on the content of chromium(VI) and nickel compounds in welding fume formed during the CMT and ColdArc welding of steels [1,3]. The analyses of the test results have revealed that a chromium(VI) content in fume increases if an arc shielding is composed of gases characterised by strong and medium oxidising properties. During CMT and ColdArc welding of chromium ferritic steel the strongly oxidising 82%Ar+18%CO_2 gas mixture caused the highest content of Cr(VI) content in fume (Fig. 10). High Cr(VI) content values were also observed for the 90%Ar+5%CO_2+5%O_2 triple-component gas mixture characterised by medium oxidising properties as well as for the argon + oxygen mixture. The low-oxidizing index mixture containing carbon dioxide (97.5%Ar+2.5%CO_2) caused a low chromium(VI) content in the fume. This is due to low oxidising ability and the presence of carbon oxide (characterised by reducing properties) in a welding arc. A low Cr(VI) content in fume during welding of the austenitic steel was tied to the use of argon as a shielding gas (Fig. 11). Tests related to nickel content in fume were carried out with three different shielding gases, i.e. argon, argon + oxygen and argon + carbon dioxide. The effect of shielding gas composition on nickel content in fume during CMT welding is presented in Figure 12.

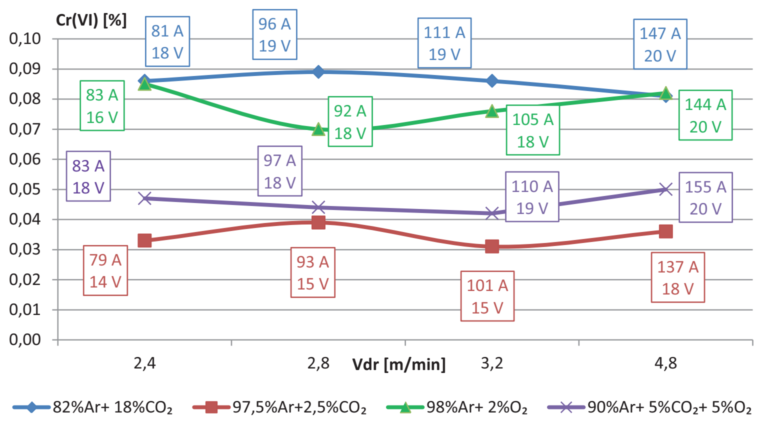

Fig. 10. Cr(VI) content in fume during ColdArc welding of X6Cr17 steel using various shielding gases [1]

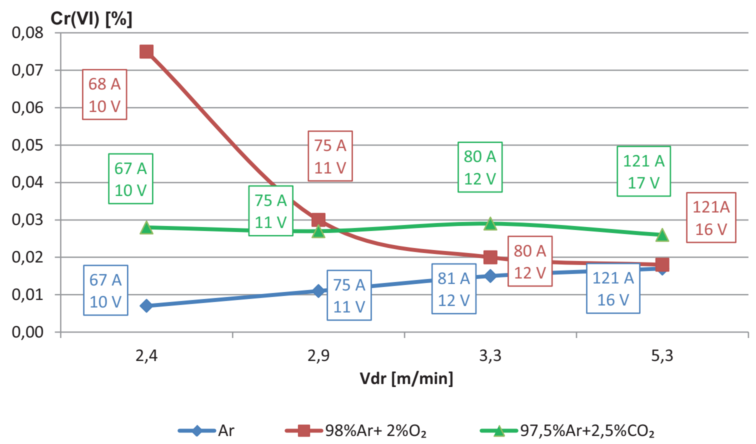

Fig. 11. Cr(VI) content in fume during CMT welding of X5CrNi18-10 steel using various shielding gases [1]

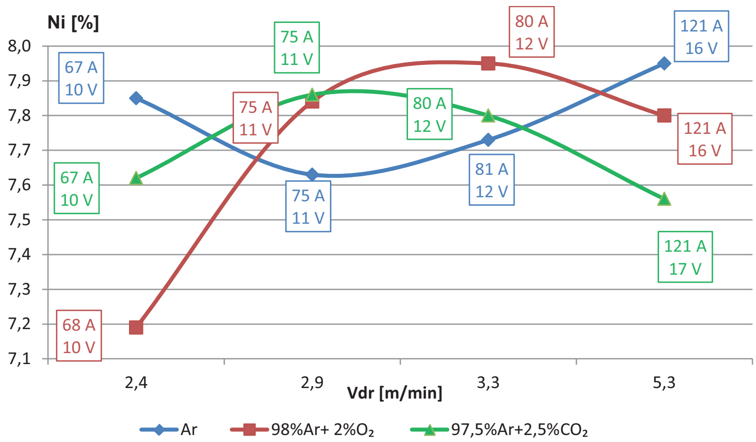

Fig. 12. Nickel content in fume during CMT welding of austenitic steel using various shielding gases [1]

Conclusions

1. The material-technological conditions of CMT and ColdArc welding of corrosion-resistant steels affect the emission of total fume and its chemical composition, in particular the content of chromium(VI) and nickel.

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2. The tests of the emission of fume and gases generated during welding of stainless steels have demonstrated a significant influence of a selected welding method on the size of pollutant emission. During CMT (Cold Metal Transfer) welding the size of fume, NO_x and CO emission is lower than that accompanying emission during ColdArc welding.

3. The lower emission of pollutants to a work environment during CMT welding of stainless steels makes this method significantly more convenient. Due to a stable arc, small number of spatters and the possible reduction of fume and gas emission, the Cold Metal Transfer method is especially recommended for improving work conditions during welding of sheets made of corrosion-resistant steels.

4. The composition of a shielding gas significantly affects the size of total fume emission as well as the emission of gases and chromium(VI) and nickel content in fume generated during CMT and ColdArc welding of stainless steels:

– reduction of fume emission during welding austenitic and ferritic steels requires the use of the $Ar+O_2$ mixture. The highest emission of fume during welding of austenitic steel was observed when pure argon was used as a shielding gas, whereas the highest fume emission during welding of chromium ferritic steel was observed when the $82\%Ar+18\%CO_2$ mixture and the $90\%Ar+5\%CO_2+5\%O_2$ triple-component mixture were used as shielding gases;
– reduction of nitrogen oxide emission during welding of corrosion-resistant steels requires the use of the $Ar+CO_2$ bi-component mixture;
– reduction of carbon oxide emission during CMT and ColdArc welding of austenitic steels requires the use of the $Ar+O_2$ mixture and pure argon as shielding gases. Also during welding chromium ferritic steels it is advisable to use the $Ar+O_2$ mixture in order to reduce carbon oxide emissions;
– chromium(VI) content in fume increases when strong and medium index oxidising gases are used as shielding gases. Mixtures with a low oxidising index, containing carbon dioxide contribute to a low chromium(VI) content;
– nickel content in fumes increases when the atmosphere of an arc has an oxidising character.

Emission of fumes and gases and fume chemical composition during CMT and ColdArc braze welding of coated steels

Testing emissions of pollutants during argon-shielded arc braze welding was carried out for four different base metals [1,4,5], i.e. DX 54D grade unalloyed steels with a zinc coating and a zinc-iron coating as well as DP600X ultra strength steel (UHSS) provided with a zinc-iron coating. The tests were conducted for different thicknesses and densities (100 g/m^2 and 140 g/m^2) of protective coatings. The coatings were also characterised by improved surface quality and had undergone oiling for better anticorrosive protection. A filler metal used in the tests was CuSi3 filler metal wire with a high copper content ($Cu \geq 95\%$). During braze welding, a base metal does not undergo partial melting and the window of current-voltage parameters is significantly narrower than during welding processes. For this reason, pollutant emission tests were carried out only for 3 different current-voltage parameter values, filler metal wire feeding rate and welding rate. The discussion of the test results refers to the impact of the grade of the material weldbrazed and the type of coating used on the size of fume and gas emission as well as on the chemical composition of fume emitted during a welding process.

Effect of anticorrosive coating on fume and gas emission during braze welding of coated steel sheets

The analysis of the test results has revealed that the greatest fume emission accompanied braze welding of sheets provided a coating

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made of zinc and iron (ZF). A zinc coating (Z) was characterised by lower values of emission for the same current-voltage process conditions and the same braze welding methods (Fig. 13, 14). The size of fume emission is also affected by the thickness of the coating, and this dependence is directly proportional, i.e. a greater thickness is connected with a greater emission of fume. Also the emissions of nitrogen and carbon oxides depend on the types of protective coatings. During ColdArc braze welding the emission of NO_x and CO was the highest for the sheet with the thicker ZF (zinc-iron) coating - DX54D ZF 140 (Fig. 15). During CMT welding the emission of nitrogen oxides was also the highest for the ZF140 coating. The highest carbon oxide emission accompanied braze welding of the sheet with the Z140 zinc coating (Fig. 16). Similarly as in the case of fume emission the thickness of a coating also affects the size of gas emission (Fig. 17). When subjected to braze welding, thicker ZF and Z coatings cause greater emissions of nitrogen and carbon oxides.

The tests have revealed that emissions of nitrogen and carbon oxides depend on the types of protective coatings, yet this correlation is difficult to define explicitly. During ColdArc braze welding the emission of NO_x and CO was the highest for the sheet with the thicker coating made of zinc and iron - DX54D ZF 140. During CMT welding the emission of nitrogen oxides was also the highest for the ZF140 coating. In turn, the highest carbon oxide emission accompanied braze welding of the sheet with the Z140 zinc coating. The size of gas emission is also strongly affected by the thickness of a coating. Similarly as in the case of fume emissions this dependence is directly proportional, i.e. in braze welding

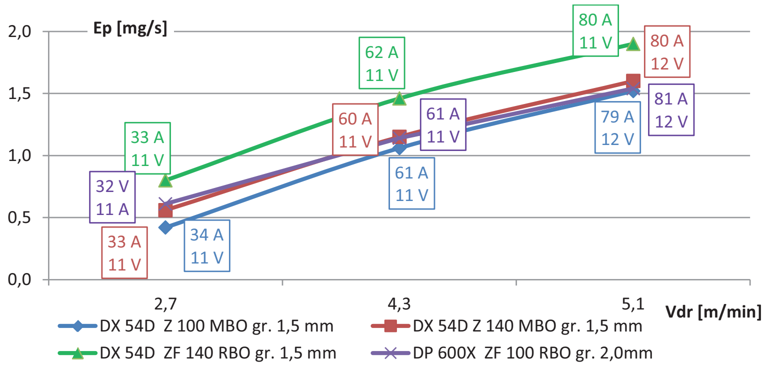

Fig. 13. Effect of protective coatings on fume emissions during CMT braze welding [1]

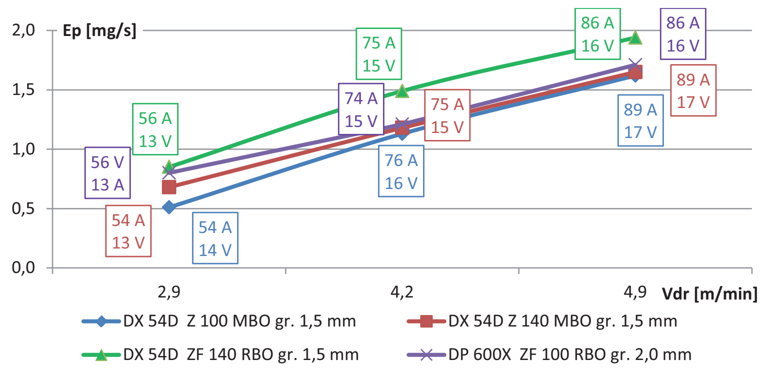

Fig. 14. Effect of protective coatings on fume emissions during ColdArc braze welding [1]

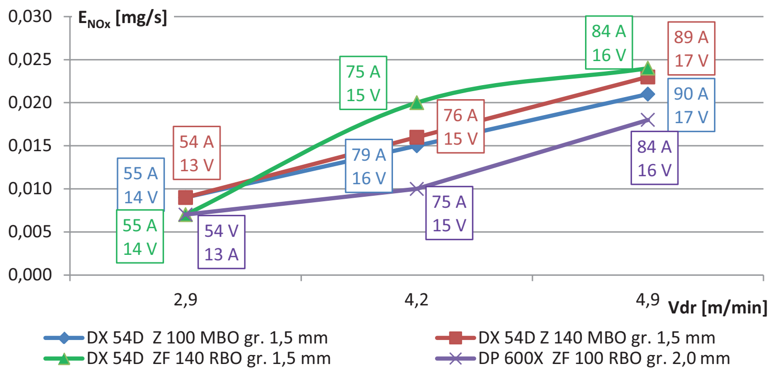

Fig. 15. Effect of protective coatings on nitrogen oxide emissions during ColdArc braze welding [1]

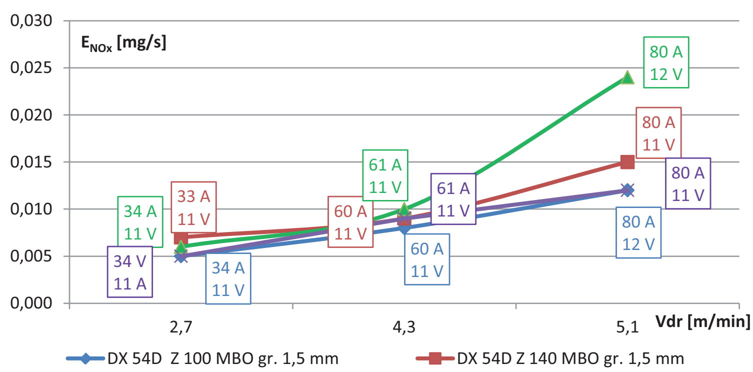

Fig. 16. Effect of protective coatings on nitrogen oxide emissions during CMT braze welding [1]

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of steel sheets provided with ZF and Z coatings an increase of a coating thickness is connected with higher emissions of nitrogen and carbon oxides.

While assessing work conditions accompanying arc braze welding of sheets having protective coatings, it is important to bear in mind a high content of zinc compounds in the fume. A coating made of the zinc-iron alloy (ZF) causes a greater zinc content in fume if compared to a zinc content related to a coating made of pure zinc (Z type). The content of zinc in the fume amounts to 42-43% during joining sheets provided with ZF coatings and 37-38% during joining sheets having Z coatings (Fig. 18). The content of zinc in the fume is also dependent on the thickness of the protective coating. Zinc contained in the protective coating is characterised by low melting (419°C) and boiling (907°C) points and starts evaporating just above 600°C [5,6]. During braze welding of galvanised sheets, zinc melting in the area of elements being joined evaporates partly with its small amount passing to liquid brazing metal [7]. If compared with MIG/MAG welding, MIG braze welding is characterised by a smaller heat input, which enables maintaining the original anticorrosive coating of a base metal in a joint area.

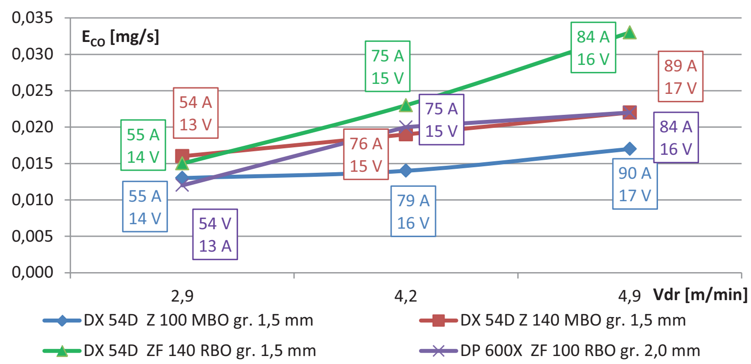

Fig. 17. Effect of protective coatings on carbon oxide emissions during ColdArc braze welding [1]

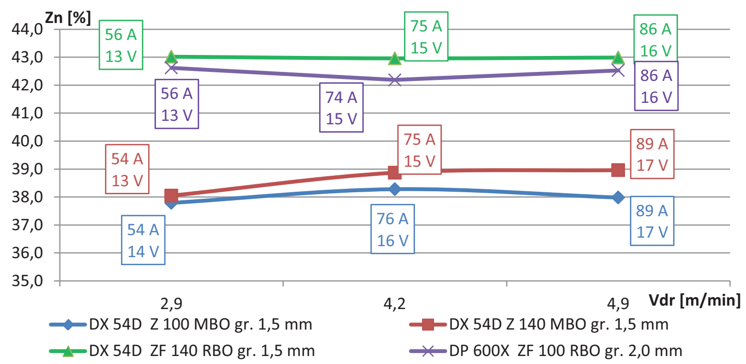

Fig. 18. Zn content in fume during ColdArc braze welding of coated sheets [1]

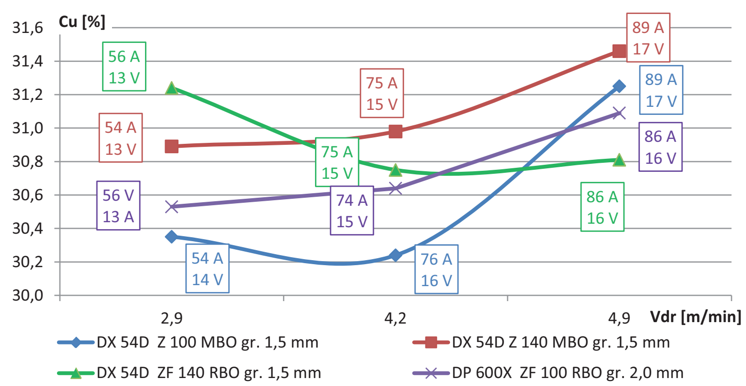

Fig. 19. Cu content in fume during ColdArc braze welding of coating sheets using CuSi3 wire with a diameter of 1.0 [1]

The test results have revealed that the main fume constituents during CMT and ColdArc braze welding are copper 29.8-31.4% (from the filler metal), zinc 37-43% (from the coating), iron 1.8-3.5% (from the ZF coating and the base metal), manganese 0.7% (from the base and filler metals) and silicon 1.3-1.7% (from the base and filler metals) [1,5].

Conclusions

1. The greatest fume emission accompanies braze welding of steel sheets with ZF coatings, i.e. made of a zinc and iron alloy. The zinc coating was characterised by lower emission values for the same current-voltage process conditions and the same braze welding methods.

2. Fume, nitrogen oxide and carbon oxide emissions depend on the thickness of Z and ZF anticorrosive coatings; this dependence is directly proportional.

3. The effect of the type of an anticorrosive coating on the chemical composition of fume generated during braze welding processes is visible while analysing

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zinc content in fume. The zinc-iron alloy coating (ZF) causes a greater zinc content in fume than the Z coating (mad of pure zinc). The content of zinc in fume stands at 42-43% during joining sheets provided with ZF coatings and at 37-38% during joining sheets having Z coatings. The content of zinc in fume also depends on the thickness of the protective coating.

Resting emissions of fume and gases during resistant welding of steel sheets provided with double-layer protective coatings

The tests focusing on emissions of pollutants during spot resistance welding were carried out for sheets with double-layer protective coating [2]. The sheets selected for the tests, i.e. ZE 36/36 and ZE 50/50 had been subjected to two-sided electrogalvanising. The second layer was an organic coating: Granocoat and Gardo Protect. The sheets were characterised by improved surface quality and the coatings had undergone oiling for better protection. The emission of pollutants was also tested for spot resistant welding of sheets with a metal alloy coating: aluminium alloy, iron and silicon, AS 120 coating. The sheet used was hot-dip aluminised with a 12 μm thick coating. The surface of the coating was additionally protected by oiling.

The steel grades selected for the tests are commonly used in metal processing and the automotive industry, as well as in the production of industrial fixtures, chemical equipment and household goods. The results of the tests are universal and relate to a vast sector processing steels with coatings.

During welding the technological process parameters such as welding current, voltage, welding energy, current flow time, pressure force and the number of welds were recorded. The tests were carried out with welding current from a 8-10 kA range, pressure force from a 250 – 350 daN range and welding time between 250 and 300 ms. The results related to the sizes of pollutant emissions during spot resistance welding of various coated sheets have made it possible to conduct a comparative analysis which included the effect of welding current on the emissions of fume, carbon oxides and nitrogen oxides. The comparison also involved the sizes of fume and gas emissions for similar technological welding conditions but different steel grades and various types of coatings.

The project implementation [2] was also connected with the carrying out the phase identification and the phase quantitative analysis of fume formed during spot resistant welding of steel sheets having protective coatings. The research also involved the analysis of organic compounds formed during welding of steel sheets with double-layer coatings as well as the determination of benzene, toluene, ethylbenzene, xylenes, phenol, cresols and polycyclic aromatic hydrocarbons.

Effect of welding current on emission of total fume and gases

Tests of fume, carbon oxide and nitrogen oxide emissions during spot resistance welding have revealed a significant effect of welding current on the size of pollutant emission; an increase in welding current caused greater emissions of total fume, carbon oxides and nitrogen oxides during welding sheets of the same thickness and with maintaining the same values of welding time and pressure force [2,8,9]. The dependence between welding current and the size of pollutant emission is common for all the types of coated materials tested. For instance, during welding of the DC04 ZE 50/50 AO + Granocoat sheet with a thickness of 1.25 mm it was observed that an increase in welding current from 8 kA to 10 kA resulted in a three-fold increase in fume (Fig. 20) and carbon oxide emissions. Particularly high emission indicators related to total fume, carbon oxides and nitrogen oxides characterised welding sheets with high welding current exceeding 10 kA. High current parameters of resistance welding cause dynamic melting and evaporation of the

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protective coating as well as the burning of the organic later; the melting of the base metal, i.e. steel, was also observed. Resistance welding processes carried out using higher current are connected with the intense expulsion of metal forming fume. The correlation between welding current and emissions of total fume, carbon oxides and nitrogen oxides may provide the basis for the technological reduction of pollutant emissions by decreasing welding current values.

Effect of welded material coating on emission of pollutants

Emissions of pollutants during spot resistance welding were carried out for five types of coatings differing in the manner of application, chemical composition, thickness and additional protection of the coating surface. Double-layer coatings are composed of a metal layer – electrolytic zinc coating (ZE type) and a thin organic coating (Granocoat or Gardo Protect types). One of the sheets tested was provided with a metal coating being an Al+Si+Fe alloy. The effect of the type of coating of the material being welded on the size of fume, carbon oxide and nitrogen oxide emissions is presented in Figures 21-23. The tests have revealed the influence of the type of a protective coating on the size of total fume and gas (CO, NO_x) emissions. The highest emission of total fume accompanied welding of LAC 320Y400T ZE50/50 OC Gardo Protect grade sheets and DC04 ZE 36/36 OC Gardo Protect grade sheets. Lower fume emission values were observed for the sheets with the Granocoat coating, i.e. HC 340 LA ZE 50/50 AO + Granocoat and DC04 ZE 50/50 AO + Granocoat. The sheet with the alloy metal coating of the Al+Si+Fe alloy type was characterised by the lowest emission of total fume (Fig. 21).

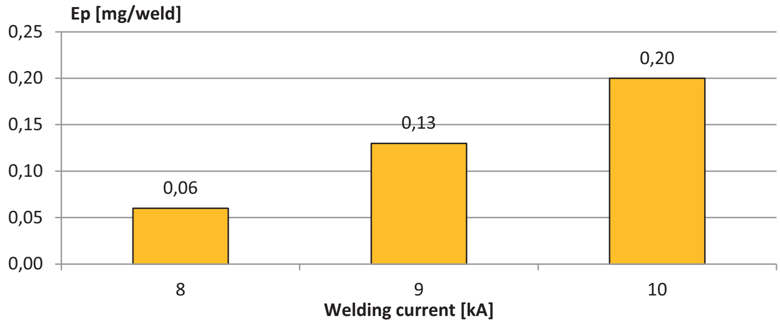

Fig. 20. Effect of welding current on total fume emission during spot resistance welding of 1.25 mm thick DC04 ZE 50/50 AO + Granocoat sheet [2]

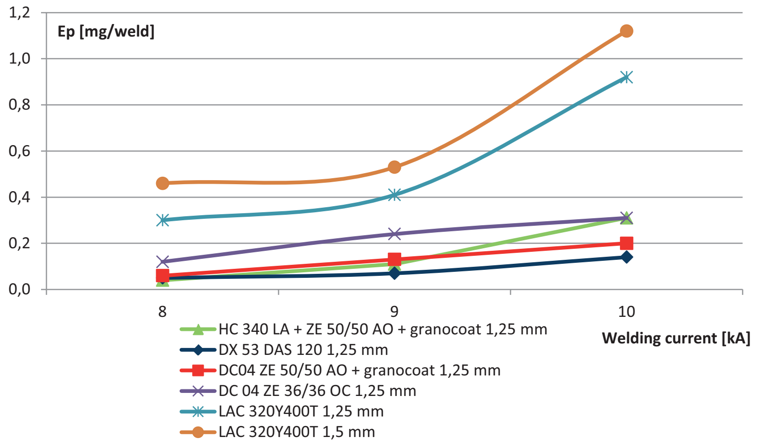

Fig. 21. Effect of protective coating type on total fume emission during spot resistance welding of 1.25mm and 1.5mm thick steel sheets [2]

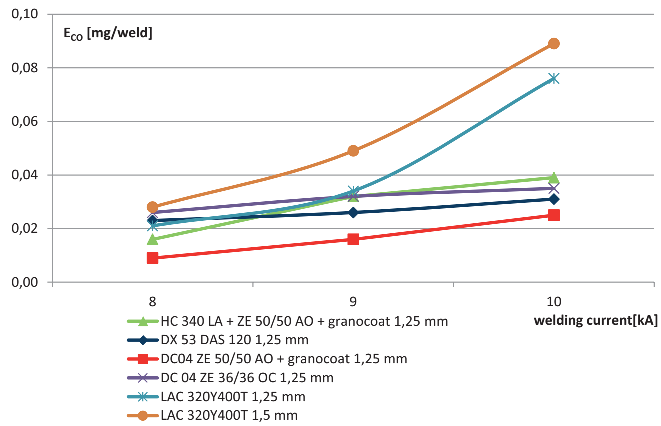

Fig. 22. Effect of protective coating type on carbon oxide emission during spot resistance welding of 1.25mm and 1.5mm thick steel sheets [2]

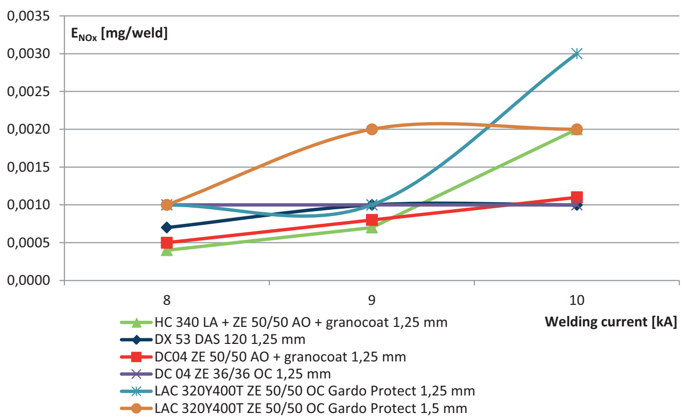

Fig. 23. Effect of protective coating type on nitrogen oxide emission during spot resistance welding of 1.25mm and 1.5mm thick steel sheets [2]

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The highest carbon oxide emission accompanied welding of the sheets with the Gardo Protect coating. In the case of Granocoat coatings and Al+Si+Fe metal coatings the indicators of CO emission are comparable. The lowest carbon oxide emission was observed during welding DC04 ZE 50/50 AO Granocoat sheets (Fig. 22). The tests have also revealed that the highest NO_x emission is connected with the Gardo Protect coating (Fig. 23).

Phase identification and quantitative phase analysis of fume formed during spot resistance welding of steel sheets with protective coatings

The phase identification of total fume formed during welding of steel sheets provided with protective coatings involved the determination of the following phase components of fume: wüstite (FeO), metallic Mn, metallic Zn, metallic Fe, ZnO, magnetite (Fe_3O_4), hematite (α-Fe_2O_3), Mn_3O_4, $FeCO_3$, metallic Al, Al_2O_3 and $MnAl_2O_4$. The identification was carried out for the following 3 sheets with double-layer protective coatings: DC 04 ZE36/36 OC Gardo Protect, HC 340 LA ZE 50/50 AO + Granocoat and DC 04 ZE 50/50 AO + Granocoat. In the fume formed during welding of sheets using 8-9 kA current it was possible to identify FeO, metallic Mn, metallic Zn, metallic Fe and ZnO in the chemical composition. In the fume formed during welding of sheets using higher current, i.e. 10 kA, it was possible to identify FeO, metallic Mn, Zn, metallic Fe, zinc oxide, magnetite Fe_3O_4, hematite α-Fe_2O_3, Mn_3O_4 and $FeCO_3$. In the fume collected from the chamber (fume settling during a welding process) it was possible to identify the following chemical composition: FeO, metallic Mn, metallic Zn, metallic Fe, zinc oxide, magnetite Fe_3O_4, hematite α-Fe_2O_3, Mn_3O_4, metallic Al, Al_2O_3, and $MnAl_2O_4$.

The chemical composition of the fume settled on the measurement filters during welding (suspended fume) for welding current from the 8 -10 kA range and the chemical composition of the fume collected from the chamber (settling fume) after welding DC 04 ZE 50/50 AO + Granocoat grade sheets is presented in Figure 24.

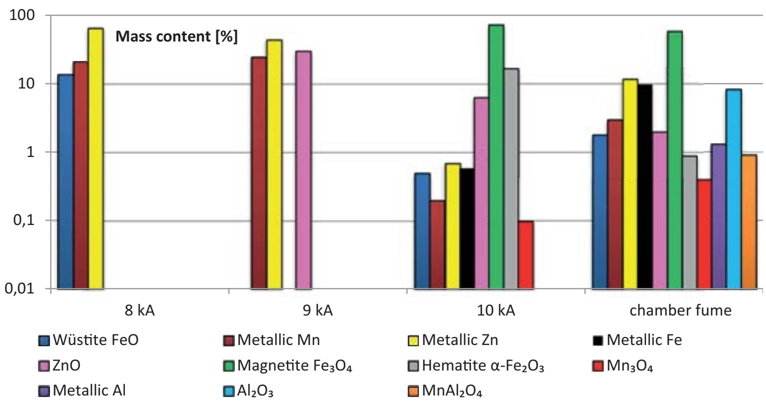

Fig. 24. Quantitative phase analysis of fume formed during spot resistance welding of DC 04 ZE 50/50 AO + Granocoat grade sheet [2]

After welding the sheets tested with the current 8 kA, the main constituent of welding fume is metallic Zn in the range from 42.8% to 65.7% [m/m]. Also, the presence of metallic Mn in the range from 12.1% to 42.2% [m/m] and of FeO in the range from 13.6% to 45.1% [m/m] was identified. After welding the sheets tested with the current 9 kA the main constituent of welding fume is metallic Zn in the range from 40.2% to 53.6% [m/m], next FeO in the range from 23% to 39.2% [m/m], and also metallic Mn in the range from 10% to 24,9% [m/m]. After welding DC 04 ZE 50/50 AO + Granocoat grade sheet, ZnO – 30.5% [m/m] was identified in the fume. In turn, welding of steel sheets having a double-layer coating using the current of 10 kA is connected with the emission of fume, the chemical composition of which is more complicated in comparison with that obtained during welding with lower current parameters. If welding is carried out with the current 10 kA, welding fume is mainly composed of (Fig. 25) the following:

- magnetite Fe_3O_4 in the range from 70.9 to 75.1% [m/m],
- ZnO in the range from 8 to 13.5% [m/m],
- hematite α-$Fe2O3$ in the range from 4.6 to 16.8% [m/m],

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– wüstite FeO in the range from 0.5 to 5.6% [m/m],
– metallic Zn in the range from 0.7 to 3.8% [m/m].

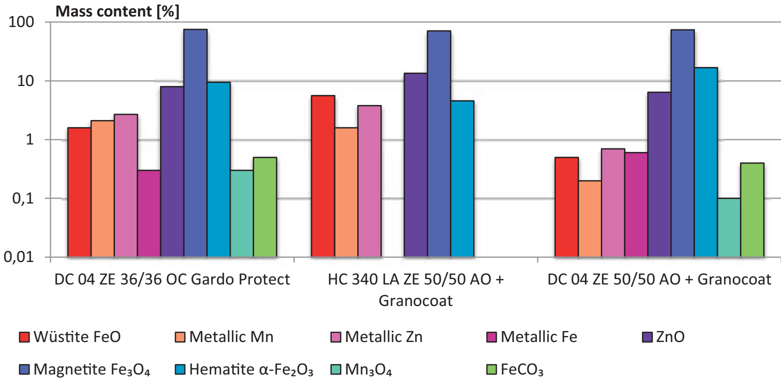

Fig. 25. Chemical composition of fume formed during resistance welding of sheets with double-layer coatings, welding current 10 kA [2]

Emission of organic substances formed during spot resistance welding of coated steel sheets

The analysis of organic substance emissions during welding of coated sheets was carried out for three groups of organic compounds [2]:
– for BTEX compounds - benzene, toluene, ethylbenzene and o,m,p-xylene,
– for phenol, o-cresol and m+p cresol,
– for polycyclic aromatic hydrocarbons – 16 PAH.

Among organic substances analysed the most hazardous for human health are benzene and polycyclic aromatic hydrocarbons (PAH). Benzene is a substance listed among carcinogenic and mutagenic substances [10]. According to IARC guidelines, benzene is regarded as a carcinogenic (group 1). Nine of the PAH identified in the tests are carcinogenic: dibenzo(a,h)anthracene (Relative Potency Factor RPF-5), benzo(a)pyrene (WWK-1), benzo(a)anthracene (RPF-0.1), benzo(b)fluoranthene (RPF-0.1), benzo(k)fluoranthene (RPF-0.1), indeno-(l,2,3-c,d)pyrene (RPF-0.1), anthracene (RPF-0.01), benzo(g,h,i)perylene (RPF-0.01) and chrysene (RPF-0.01) [11].

The tests revealed that resistance welding of sheets with Granocoat organic coatings is accompanied by the formation of welding fume characterised by high benzene emission. During welding of steels sheets having Gardo Protect coatings with current from the range tested (8-9 kA), the emission of benzene is approximately 10 times lower (Fig. 26). The highest RPF emission was identified for fluorene, phenanthrene and chrysene. Welding fumes also contained benzo(a)pyrene, i.e. a toxic and carcinogenic (cat. 2) and mutagenic (cat. 2) substance listed among carcinogenic and mutagenic substances. The highest emission of benzo(a)pyrene accompanied welding of HC 340 LA ZE 50/50 AO + Granocoat sheets. Particularly high emission of these organic substances was observed during welding of sheets provided with ZE+Granocoat double-layer coatings. The emission of such substances to a work environment is connected with the decomposition of protective coatings and oil applied on the surface of sheets (Fig. 27).

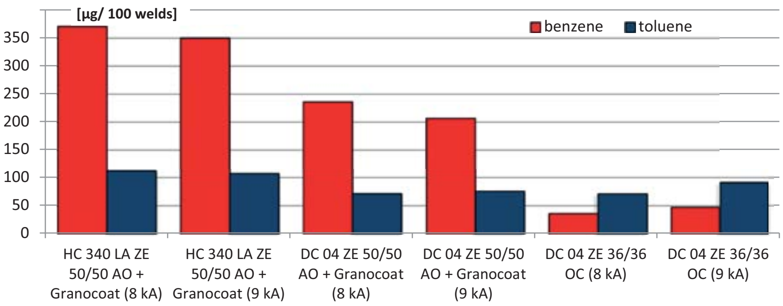

Fig. 26. Emission of benzene and toluene during resistance welding of sheets having double layer coatings (ZE+organic coating) [2]

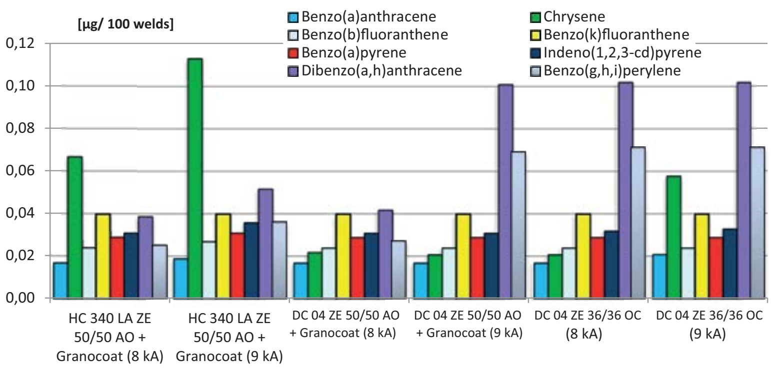

Fig. 27. Emission of polycyclic aromatic hydrocarbons during spot resistance welding of sheets with double layer coatings (ZE + organic layer) [2]

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Concluding remarks

1. The tests of total fume, nitrogen oxide and carbon oxide emissions during spot resistance welding of sheets with double-layer coatings (ZE+Granocoat/Gardo Protect) revealed the effect of welding current on the size of pollutant emissions; an increase in welding current causes a greater emission of total fume, nitrogen oxides and carbon oxides during welding of sheets having the same thickness and being welded for the same time and exposed to the same pressure force. The dependence between welding current and the emission of pollutants was observed for all the grades of materials with double-layer coatings tested.

2. The tests have revealed the effect of the type of a protective coating on the size of total fume, nitrogen oxide and carbon oxide emissions; under similar technological welding conditions, greater pollutant emissions were characteristic of the steel sheets with the ZE coating (electrogalvanised sheet) + Gardo Protect organic coating. The hot galvanised steel sheet with the Al+Si+Fe alloy metal coating was characterised by a lower total fume emission.

3. The main chemical constituents of welding fume formed during resistance welding of coated steel sheets are the following:

- for welding current between 8 and 9 kA: metallic Zn, metallic Mn, wüstite (FeO) and ZnO;
- for welding current of 10 kA: magnetite Fe_3O_4, ZnO, hematite α-Fe_2O_3, wüstite (FeO), metallic Zn.

4. The main chemical constituents of settling welding fume formed during resistance welding of coated steel sheets are magnetite (Fe_3O_4), metallic Zn, metallic Fe, ZnO, wüstite (FeO), metallic Mn, hematite (α-Fe_2O_3) as well as Al_2O_3, metallic Al and Mn_3O_4.

5. The tests have revealed the effect of the type of a double-layer protective coating on the emissions of organic substances; welding fume formed during resistance welding of sheets having Granocoat organic coatings is characterised by high benzene and toluene emission.

6. Welding fumes were also identified as having polycyclic aromatic hydrocarbons. The tests have revealed the presence of nine carcinogenic substances, i.e. dibenzo(a,h)anthracene, benzo(a)pyrene, benzo(a)anthracene, benzo(b)-fluoranthene, anthracene, benzo(k)fluoranthene, indeno(l,2,3-c,d)pyrene, benzo(g,h,i)perylene and chrysene.

7. The formation of carcinogenic substances during resistance welding of coated sheets is ascribed to the temperature-triggered decomposition of the oil layer as well as with melting and the decomposition Gardo Protect and Granocoat coating layers. Particularly high emission of these organic substances accompanied welding of sheets provided with ZE+Granocoat double-layer coatings.

Summary

Welding and braze welding techniques which, in the aspect of the tests related to occupational safety, were the subject of the research "Assessment of Chemical, Fume and Physical Hazards in the Work Environment Related to Innovative Methods for Joining Various Structural Materials as an Activity Supporting the Assurance of Safe Work Conditions" are technologies of today and tomorrow as regards joining various structural materials in many industries. These joining methods are referred to by the European Welding Federation as Cool, Clean and Clever (3C) and are perceived as a group of production welding processes characterised by innovativeness, constant development and improvement of equipment, technologies and materials as well as processes offering possibilities of continuous improvement of work conditions. Research into the work environment carried out at Instytut Spawalnictwa have enabled the identification, analysis and assessment of chemical and fume hazards accompanying low-energy arc welding and braze welding as well as resistant welding of modern structural materials. This research has helped to determine the

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possibilities of optimising these technologies in order to improve work conditions and occupational safety. The tests have enabled the development of technical (material-technological) and organisational recommendations concerning the prevention of hazards during welding and braze welding. The recommendations made have taken into consideration the analysis of all tests results and formulated detailed conclusions referring to individual joining methods and chemical, fume and physical hazards [4,9] and are intended for specialists in welding techniques who, in collaboration with occupational safety services in production facilities, will select base metals, technological parameters and joining methods while arranging safe workplaces.

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