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JOINING UFG COPPER BY MEANS OF THE W2Mi MACHINE

Joining metals with ultra-fine grains (UFG) is very difficult. UFG metals have a grain size of less than 1 µm. Exceeding the recrystallization temperature causes the growth of ultra-fine grains and degradation of the material's mechanical properties. The process temperature is influenced by the amount of energy supplied to the joint, which depends on the power and time. Conventional machines are not adapted to effectively conduct the process in extremely short friction times. For this reason, this article presents the welding process on the W2Mi prototype machine. The design of this machine allows the joining of UFG metals in less than 100 ms. UFG material produced using the hybrid SPD (Severe Plastic Deformation) process from technically pure CW004A (Cu-ETP) copper was used for welding tests. The joint obtained on the W2Mi machine did not show any significant degradation signs of mechanical properties. At the same time, an increase in microhardness in the joint area by approximately 4% was noticed. The obtained results prove that the process of joining UFG metals was successfully carried out.

Keywords: Rotation Friction Welding; Ultra-Fine Grained copper; hybrid SPD; ECAP

1. Introduction

Rotational friction welding (RFW) belongs to the group of solid-state welding methods [1]. A characteristic feature of the RFW method is the joining of axisymmetric products below their melting temperature. The drive system for the rotational movement of the sample in the RFW process, which supplies energy to the resulting joint, is based on a motor driven or flywheel [2]. A system based on a motor-drive is called direct-drive. This drive system keeps the rotational speed constant until braking begins. The second system based on flywheel is called inertia friction welding (IFW). When using a flywheel, the mechanically connected sample is accelerated to the set rotational speed, and then the drive is disconnected. The kinetic energy collected in the flywheel allows the specimens to be welded while the rotation speed decreases after the samples come into contact. In both cases, the rotational drive system causes rotation of one of the samples, while the other remains stationary. After reaching the set rotational speed, the samples are brought closer to each other until their surfaces touch. From this point the friction stage begins. As a result of this process, energy is supplied to the joint according to formula Eq. (1):

$$E = \int_0^t \frac{2}{3} \mu F r \frac{\pi n}{30} dt \; [\mathrm{J}] \qquad (1)$$

where, F [kN] – force, n [rpm] – the difference in the rotational speed of the specimens, μ [-] – friction coefficient, r [mm] – specimen radius.

During this stage, the rotational speed decreases as a result of initiating braking while exerting force. This stage lasts until the friction between the front surfaces of both samples ends. Then the upsetting stage begins, in which the pressing force between both samples increases. After the set time, shortening or reaching the set force, the process ends. The RFW method enables effective joining of various materials, including aluminum alloys AA20™ [3], AA6061 [4], AA7075-T651 [5], 304 austenitic stainless steel [6], titanium Ti–6Al–4V [7], AA2219 to 304 stainless steel [8], and various materials, e.g. SA 213 T12 to SA 213 F12 low alloy steel [9], AA6082 to Ti-6Al-4V [10]. A separate group of materials are metals with ultra-fine grains (UFG), which structure degrades above the recrystallization temperature. Friction welding, due to its process characteristics, can join these materials at a temperature much lower than other welding methods [11]. The RFW method allows lowering this temperature to around the recrystallization temperature with appropriate selection of process parameters. In the recent years, tests have been carried out on joining UFG material from steel [12], aluminum [13] and copper [14]. In all studies, the mechanical properties degradation of the UFG material in

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the joint region was noted. The loss of properties is related to the amount of energy generated during process. The lower the energy, the lower the degradation of properties in the joint area, which is mainly related to the temperature of the process [15] and the shorter the duration of its exposure. This article will present research aimed at proving the possibility of joining CW004A UFG copper without a significant loss of mechanical properties in the joint area using the W2Mi prototype machine.

2. W2Mi machine

The prototype machine was built to combine the best features of rotary friction welding and pressure welding. In the first phase of the process, rotation of the sample, which causing friction, is intended to remove the top layer of material. This exposes clean metallic surfaces and eliminates roughness. An additional effect is a temperature increase in the joint area as a result of the supply of energy. This increase facilitates plastic deformation of the material and obtaining a joint. In the case of UFG materials, the recrystallization temperature cannot be exceeded, which would result in a degradation of mechanical properties. Therefore, the design of the W2Mi prototype machine (Fig. 1) allows for minimizing the friction and upsetting time. This reduces the amount of energy supplied to the joint area, which significantly reduces the process temperature. Shortening the time of the friction stage and creating the initial connection, there is a very large increase in the pressure force as in pressure welding. The design of the machine allows for obtaining high force values in a very short time. These process conditions are important in the second phase of the process, when the entire metallic surfaces are brought closer to an atomic distance, creating the final joint. This strategy is possible thanks to the non-standard operating parameters of the machine, which allows for an effective connection while minimizing the energy input.

Process with the described strategy was possible due to the use of a rigid kinematic chain in the construction of the welding machine. The W2Mi welder is built in a vertical arrangement, i.e. the axis of the welded specimens is vertical. The upper specimen is rotated around the axis using an electro-spindle. The electro-spindle is powered by an inverter, which allows for a smooth change in the rotational speed of the upper specimen. During joining, the upper specimen does not change its vertical position. The lower component of the friction welding machine is responsible for bringing the welded elements closer together during the process. The main mechanism of the lower component of the machine is the wedge mechanism. The wedge mechanism consists of two wedges. The movement of the upper wedge, which moves vertically, is caused by the movement of the lower wedge, which moves horizontally. A rolling screw mechanism causes the horizontal movement of the lower wedge. The screw mechanism is driven by a servo drive. By using rolling guides in the wedge mechanism and a rolling screw in the wedge mechanism drive, high efficiency and high stiffness of the lower component were achieved. Additionally, the lack of flexible elements in the kinematic chain means that fast changes in the rotational speed of the servo drive cause rapid changes in the position of the lower component of the machine. The presented operation of the lower subassembly makes it possible to obtain large, rapidly increasing pressure forces on the welded elements. At the same time, controlling the rotational speed of the electro-spindle and the special design of the handle of the lower specimen allow for shortening the friction time. The special design of the W2Mi machine, the servo drive used, and the control method make it possible to obtain parameters that are difficult or impossible to obtain in other friction welders [16,17] that are equipped with a hydraulic [18,19] or pneumatic drive.

The big advantage of the discussed W2Mi machine is its modular structure. This means that by replacing modules, the operating characteristics and range of parameters can be changed.

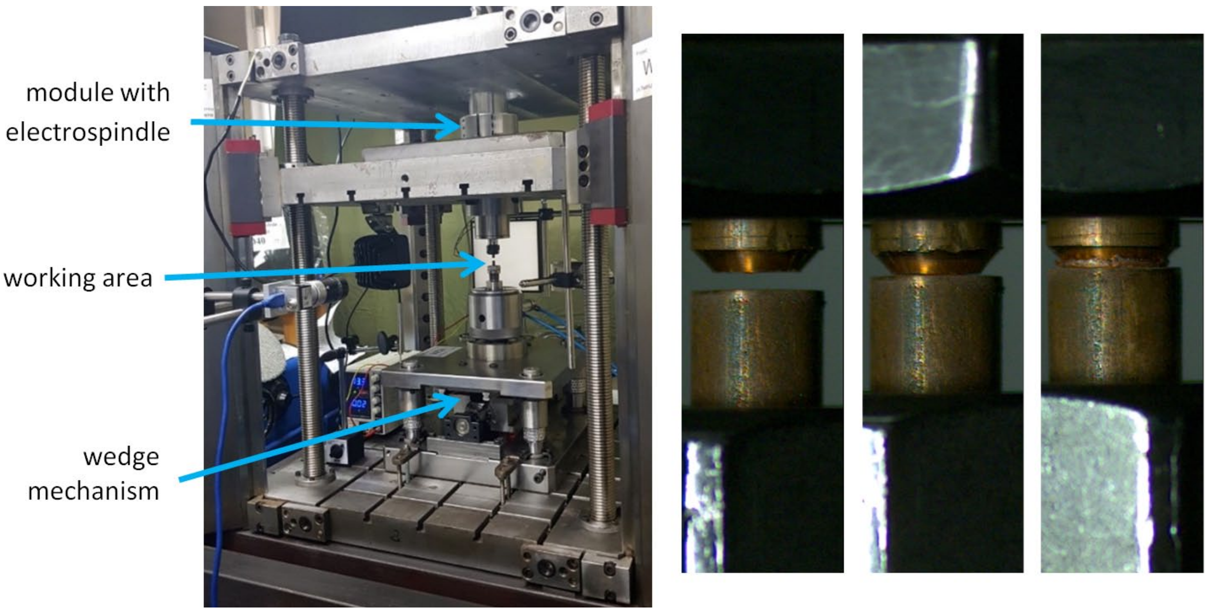

Fig. 1. W2Mi machine and close-up of the working area at various stages of the welding process

Moreover, various processes can be carried out on this machine. For this reason, the name of the machine is closely related to the modules currently used. This research presents a system of modules described by the symbol W2Mi. The first letter indicates the currently running process on the machine. The number after the first letter indicates the modules for a given process. Modules can have different parameters. Changes in characteristics of the machine's operation and the range of parameters can be obtained by replacing the modules. The letter "M" does not change and denotes a machine. The last lowercase letter refers to the sensor system and characteristics of the process. For the current modules system, the marking takes the form "W" as the welding process, "2" as welding set no. 2, "I" as a power pulse introduced into the joint limiting the friction time and energy to the necessary minimum.

3. Material

The materials used in the research were technically pure copper for general electrical purposes (EN 13601 standard) with an ultra-fine grained structure (UFG) obtained from the CW004A (Cu-ETP) coarse-grained (CG) base material in R250 condition. Coarse-grained pure copper CW004A material was used in preliminary welding tests on the W2Mi machine. It was used to select process parameters that provide the minimum amount of energy at which the resulting joint does not show any significant signs of degradation of mechanical properties. Based on the results obtained, it was possible to carry out the welding process using UFG material. The UFG structure is characterized by a grain size below 1 μm and a large angle of grain disorientation. This structure can be obtained by subjecting the material to large plastic deformation. Methods of producing the UFG structure based on this assumption are called Severe Plastic Deformation (SPD) [20]. One of the most popular SPD methods is equal channel angular pressing (ECAP) [21]. When pressing the material through the angular channel, large shear deformations are created, which result in effective grain refinement [22]. In order to create the UFG structure in CW004A copper, a special technological process called hybrid SPD was created, which is presented in Fig. 2. It is based on the 2-turn ECAP operation [23], which allows obtaining the largest deformations among other metal forming operations creating hybrid SPD. The created technological line with all used parameters allows for obtaining a material with unique properties and structure. First a rod with a diameter of ∅15 mm was upset to a diameter of ∅20 mm and then co-extruded to a cross-section of 8x8 mm, which allowed to obtain a high value of initial deformation before ECAP ($\varepsilon = 2.5$). Then, samples with a cross-section of 8×8 mm were subjected to the mtECAP (multi turn ECAP) process four times with a 2x110° channel and then co-extruded to diameter of ∅6 mm, obtaining the resulting total strain of $\varepsilon = 10.1$ and a grain size of less than 1 μm. The implemented technological process allowed an increase in the tensile strength of the CW004A material from approximately 255 MPa to 495 MPa.

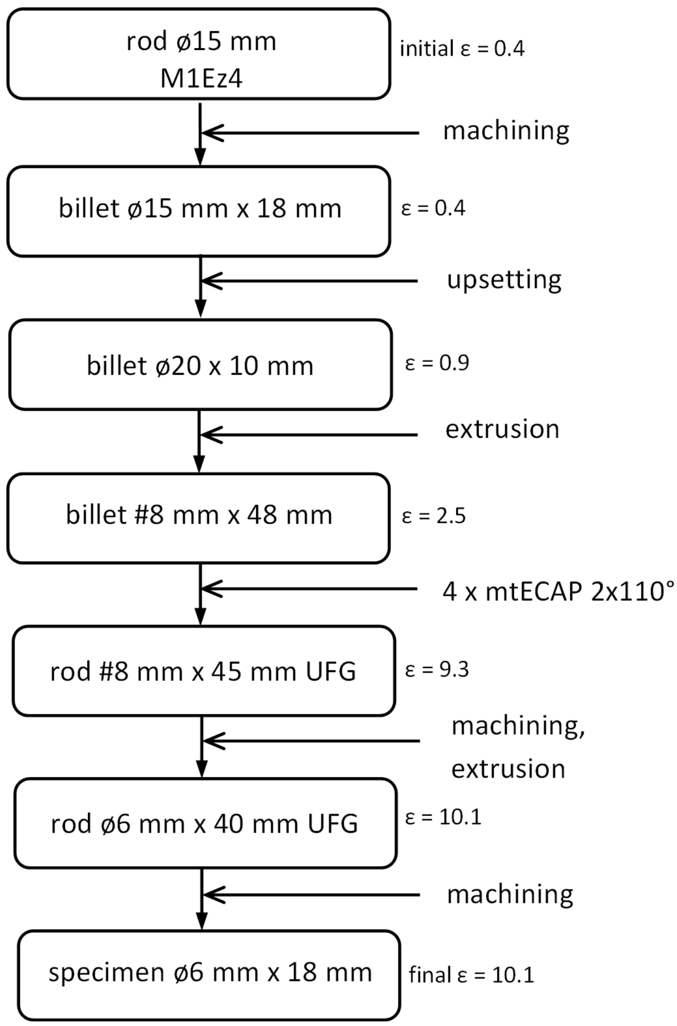

Fig. 2. Hybrid SPD process for preparing the UFG copper rods

4. Experiment

Using the W2Mi machine, the influence of rotational speed on the microhardness in the joint area, as well as the tensile strength of the joint itself, was tested. During tests on a conventional friction welding machine, the joining mechanism of the UFG material was analyzed [14]. It was found that it is necessary to minimize the fricton time for relatively high rotational speeds while maintaining high pressure. Too much energy supplied to the joint causes an increase in the process temperature and degradation of the properties of the UFG material. Minimizing the energy supplied to the joint can be achieved by reducing the friction time. For this reason, a lower temperature should affect the welded UFG material. In turn, high pressure values allow the metal surface to approach at an atomic distance while preventing discontinuities in the joint. For all welding tests, the initial distance between the sample faces was 0.7 mm, and the displacement of the lower sample during the process was set to 1.5 mm with a speed of ~1,2 mm/s. Therefore, the shortening of the sample pair was 0.8 mm after the process. First, the welding process of CW004A CG copper samples was carried out. The resulting upsetting force obtained during the process reached approximately 9 kN. The friction time has been reduced to a minimum enabling the removal of the top layer of material. It was approximately 80 ms. The process was carried out at three speeds: 7500 rpm, 9000 rpm and 10500 rpm. All process W2Mi setting parameters are presented in TABLE 1.

TABLE 1

W2Mi process setting parameters

No.	Denotation	Material	Rotational speed	Shor- tening	Displacement speed
1	CG 7500	CG	7500 rpm	0,8 mm	1,2 mm/s
2	CG 9000	CG	9000 rpm		
3	CG 10500	CG	10500 rpm		
4	UFG 7500	UFG	7500 rpm		
5	UFG 9000	UFG	9000 rpm		

The RFW process results in grain refinement and increases the properties of the CW004A CG material in the joint. In order to determine the increase in the mechanical properties of the joint and later compare it to CW004A UFG, it was necessary to obtain a reduced cross-section in this area. In each pair, the driven sample was chamfered to a diameter of ∅4 mm, as shown in Figs. 3a and 3b. This enabled stress concentration in the weld area (Fig. 3c) and limited the influence of the parent CG material with weaker mechanical properties on the result of the joint test. Welding the chamfered CW004A CG specimens ensured a reduction in the cross-section in the joint area. This made it possible to mount them directly on the universal testing machines and carry out the test without the need to perform additional operations after the process that changed the cross-section of the CG material specimens in the joint area. In order to maintain the same process parameters and cross-section area for the CW004A UFG material, the same specimen chamfered geometry was kept. Based on the results obtained, it was decided to carry out the friction welding process of the CW004A UFG material at rotational speeds of 7500 rpm and 9000 rpm (TABLE 1). While maintaining the same sample shortening, the force in the process reached 13.5 kN. This is due to the increased strength properties of this material compared to CW004A CG copper. UFG metals do not increase their mechanical properties in the joint like CG metals. Therefore, turning the chamfered CW004A UFG specimens on a lathe to a diameter of ∅4 mm on a length of 6 mm in the joint area after the welding process will not cause rupture outside the joint during a typical uniaxial tensile test. This allowed to determine the strength of the joint during a uniaxial tensile test and show the rupture geometry. The remaining specimens after the welding process were subjected to hardness measurements in the joint without turning on a lathe.

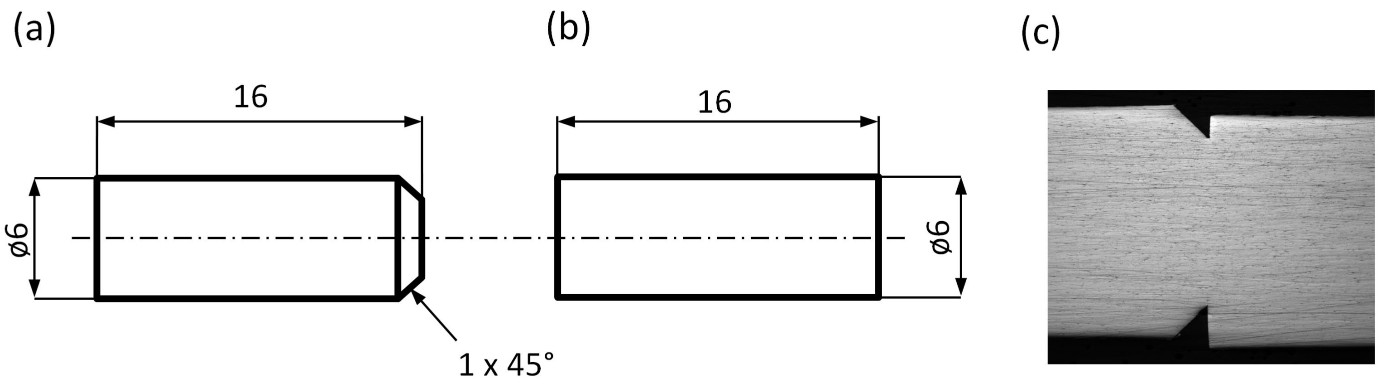

Fig. 3. Dimension of driven (a) and the lower (b) samples and cross section of the joint area (c)

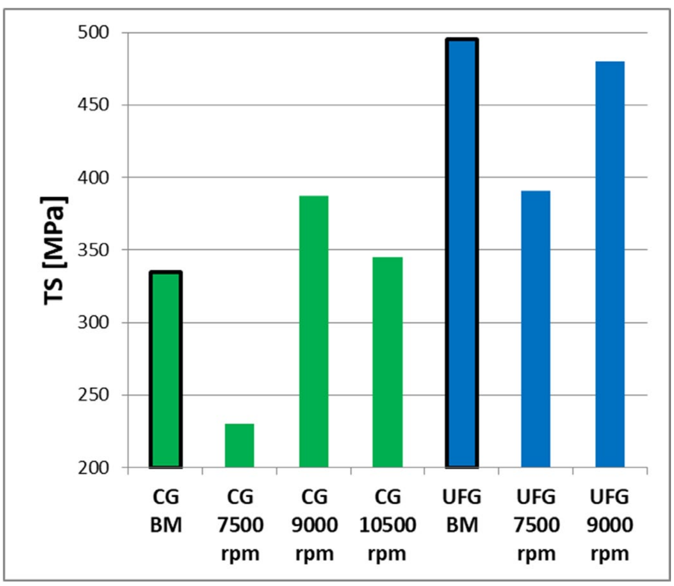

Fig. 4. Tensile strength for base material (BM) and obtained joints

5. Results

All results obtained in the uniaxial tensile test are shown in Fig. 4. Uniaxial tensile tests of CW004A CG copper joints showed that the highest strength was achieved at a rotational speed of 9000 rpm. In this test, the tensile strength (TS) reached 387 MPa. For comparison, the tensile strength of CW004A CG copper base material (BM) was 334 MPa. The joint strength for rotational speed of 7500 rpm showed a decrease. A result of 230 MPa was achieved, which was significantly lower by 104 MPa than the CW004A CG base material. Probably too low rotational speed did not allow sufficient exposure of clean metallic surfaces and elimination of roughness, which ultimately led to the formation of discontinuities in the joint area. The strength of the joint obtained when welding at a rotational speed of 10,500 rpm reached 345 MPa, which is slightly above the tensile strength of the CG base material.

Tests carried out on UFG copper confirmed the obtained relationships. The strength of the joint obtained at a speed of 7500 rpm was 391 MPa, and at a speed of 9000 rpm it was 480 MPa. The CW004A UFG base material obtained a value of 495 MPa. This means that the strength of the joint obtained at a speed of 9000 rpm is almost at the same level as that of the UFG base material. Photos of the CW004A UFG specimens after rupture and their tensile strength are shown in Fig. 5.

The microhardness measurement on the NEXUS 423D hardness tester was another test to determine the mechanical properties of the CW004A UFG copper joint. For this purpose, microsections of the samples were made along their axis. On each sample, 21 measurements were made in the sample axis, spaced 0.2 mm apart, which gives a measurement over a length of 4 mm. The central one was located in the middle of the weld. The microhardness results were averaged from three measurements. Testing of the UFG copper base material showed an average microhardness value of 136 HV02. This result was confirmed by measurements on welded samples outside the joint area. Microhardness measurement for the sample obtained at a rotational speed of 9000 rpm does not show any significant changes in hardness (Fig. 6). Another test carried out on a sample obtained at a speed of 7500 rpm showed a slight increase in microhardness to the level of 142 HV02. This represents an increase in microhardness by approximately 4% compared to the UFG base material.

6. Discussion

The carried-out tests showed a significant impact of rotational speed on the mechanical properties of the CW004A UFG copper joint. The results obtained from the uniaxial tensile and microhardness tests proved that the W2Mi prototype machine allows the joining of UFG metal without a significant decrease in strength properties in the joint area at 9000 rpm rotational speeds. This is due to the supply of a small amount of energy to the joint, which means that the recrystallization temperature is probably not exceeded. At the same time, the material in the joint area is subjected to large deformations resulting from the high upsetting force and shear caused by the friction of the specimen's front surfaces. At the same time, it was shown that the joint at a lower rotational speed had a much lower tensile strength than the UFG base material. This means that for given process parameters there is a certain critical speed below which the conditions for appropriate material joint are not met. These conditions include exposure of clean metallic surfaces, shearing

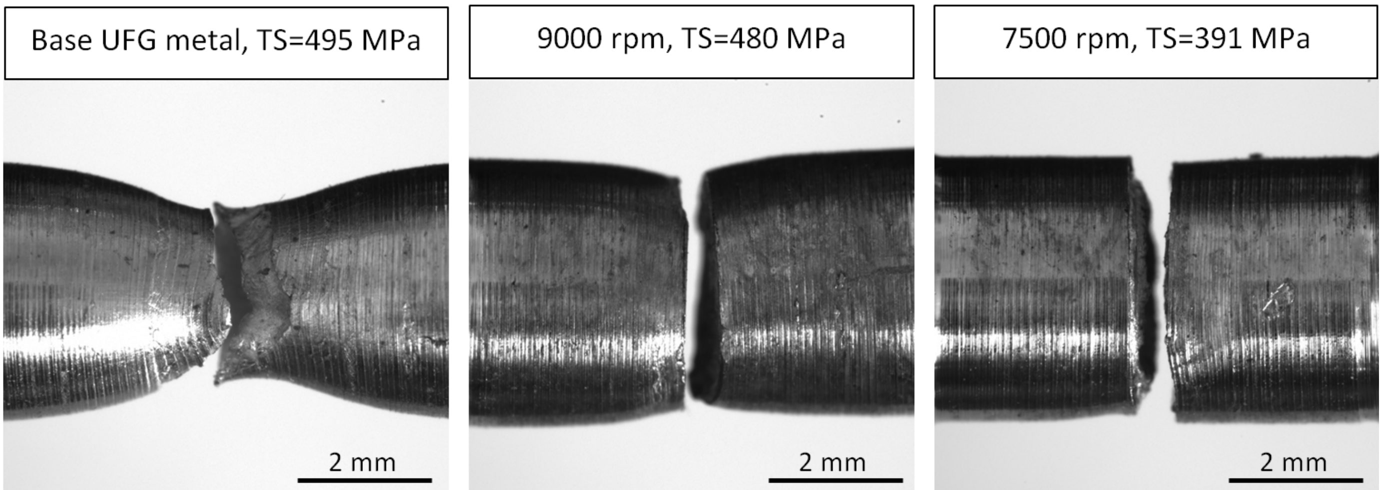

Fig. 5. UFG specimens after tensile test and their tensile strength

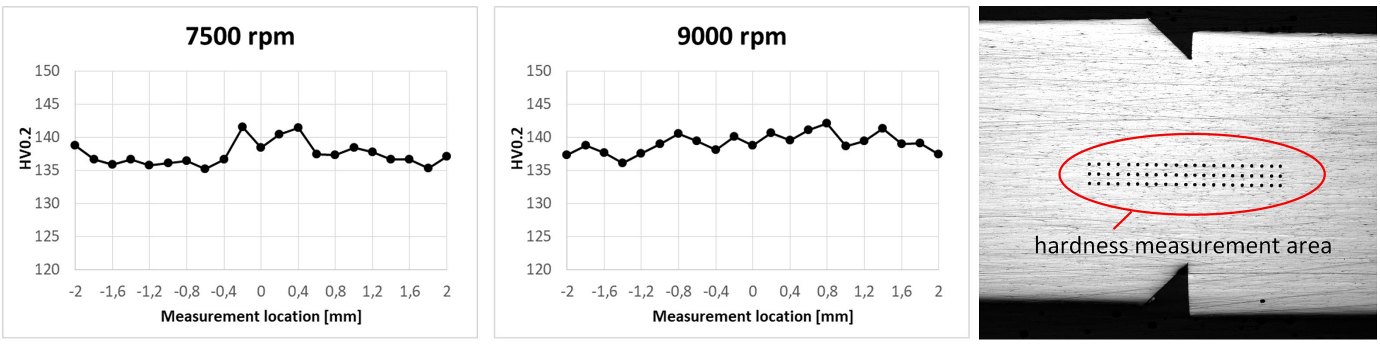

Fig. 6. Microhardness distribution for 7500 rpm, 9000 rpm and microhardness test area

of roughness and an increase in process temperature remaining below the recrystallization temperature. Increasing the rotational speed from 7500 to 9000 rpm resulted in an increase in the amount energy of welding, and the strength of welded joint condition close to the base material were met. This resulted in a joint strength value that was only 3% below the strength of the UFG base material. The presented results confirmed the possibility of joining UFG materials without any significant degradation of mechanical properties in the joint area. Moreover, an increase in microhardness could be achieved in this region. Obtaining these results was possible based on the unique operating characteristics and range of parameters of the W2Mi machine. Thanks to this, it is possible to propose a new strategy for joining materials based on short process times and high-pressure forces. In particular, for materials with an ultra-fine-grained structure, a low-energy strategy, difficult to achieve with conventional machines due to their construction and technical solutions, may open up the possibility of creating complex and long products.

7. Conclusions

Joining UFG materials requires non-standard machine operating parameters. The design of the machine should enable welding in a short time and with high pressure. Only this strategy allows the process to be carried out without grain recrystallization in the UFG metal. Based on the tests carried out on the W2Mi machine, the following conclusions can be drawn:

- The use of hybrid SPD made it possible to produce bars with an ultra-fine-grained structure from CW004A copper.
- Welding tests carried out on the W2Mi machine showed that it is possible to join UFG materials without any significant loss of mechanical properties in the joint area.
- The rotational speed influences the obtained microhardness. At speeds below 9000 rpm, there is a noticeable increase in microhardness in the joint area compared to the CW004A UFG base material.
- The appropriate speed for joining the specimens from UFG copper bars, presented in the article, is 9000 rpm. Below this speed, the tensile strength of the joint decreases.
- The design of the W2Mi machine enables effective friction welding with extremely short friction times and high pressing force.
- Reducing the friction time to the necessary minimum allowed for reducing the amount of energy supplied to the joint and maintaining the mechanical properties of UFG copper.

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REFERENCES

[1] A. Vairis, G. Papazafeiropoulos, AM. Tsainis, A comparison between friction stir welding, linear friction welding and rotary friction welding. Adv. Manuf. **4**, 296–-304 (2016). DOI: https://doi.org/10.1007/s40436-016-0163-4

[2] W. Li, A. Vairis, M. Preuss, T. Ma, Linear and rotary friction welding review. International Materials Reviews **61**, 2, 71-100 (2016). DOI: https://doi.org/10.1080/09506608.2015.1109214

[3] P. Li, S. Wang, Y. Xia, X. Hao, Z. Lei, H. Dong, Inhomogeneous microstructure and mechanical properties of rotary friction welded AA2024 joints,. Journal of Materials Research and Technology **9** (3), 5749-5760 (2020). DOI: https://doi.org/10.1016/j.jmrt.2020.03.100

[4] X. Li, J. Li, F. Jin, et al., Effect of rotation speed on friction behavior of rotary friction welding of AA6061-T6 aluminum alloy. Weld World **62**, 923-930 (2018). DOI: https://doi.org/10.1007/s40194-018-0601-y

[5] P. Hariprasath, P. Sivaraj, V. Balasubramanian, A Critical Assessment on Rotary Friction Welded High Strength Armor Grade Aluminum Alloy Joints. Phys. Metals Metallogr. **122**, 1401-1408 (2021). DOI: https://doi.org/10.1134/S0031918X21130044

[6] K. Zhang, X. Qian, J. Chen, J. Chen, H. Lu, Non-monotonic evolution of microstructure and fatigue properties of round bar–plate rotary friction welding joints in 304 austenitic stainless steel. Materials & Design **224** (2022). DOI: https://doi.org/10.1016/j.matdes.2022.111400

[7] H.Y. Chen, L. Fu, W.Y. Zhang et al., Radial Distribution Characteristics of Microstructure and Mechanical Properties of Ti–6Al–4V Butt Joint by Rotary Friction Welding. Acta Metall. Sin. (Engl. Lett.) **28**, 1291-1298 (2015). DOI: https://doi.org/10.1007/s40195-015-0325-6

[8] Z. Dang, G. Qin, J. Wang, Bonding mechanism and fracture behavior of inertia friction welded joint of 2219 aluminum alloy to 304 stainless steel. Materials Science and Engineering: A, **866** (2023). DOI: https://doi.org/10.1016/j.msea.2023.144641

[9] R. Selvaraj, K. Shanmugam, P. Selvaraj, B. Prasanna Nagasai, V. Balasubramanian, Optimization of process parameters of rotary friction welding of low alloy steel tubes using response surface methodology. Forces in Mechanics **10**, (2023). DOI: https://doi.org/10.1016/j.finmec.2023.100175.

[10] M. Meisnar, S. Baker, J.M. Bennett, A. Bernad, A. Mostafa, S. Resch, N. Fernandes, A. Norman, Microstructural characterisation of rotary friction welded AA6082 and Ti-6Al-4V dissimilar joints. Materials & Design **132**, 188-197 (2017). DOI: https://doi.org/10.1016/j.matdes.2017.07.004

[11] Ł. Morawiński, T. Chmielewski, L. Olejnik, G. Buffa, D. Campanella, L. Fratini, Welding abilities of UFG metals. AIP Conf. Proc. 2 May 2018, 1960 (1): 050012.

[12] B. Skowrońska, T. Chmielewski, W. Pachla, M. Kulczyk, J. Skiba, W. Presz, Friction weldability of UFG 316L stainless steel. Arch. Metall. Mater. **64**, 1051-1058 (2019).
DOI: https://doi.org/10.24425/amm.2019.129494

[13] M. Orłowska, L. Olejnik, D. Campanella, G. Buffa, Ł. Morawiński, L. Fratini, M. Lewandowska, Application of linear friction welding for joining ultrafine grained aluminium. J. Manuf. Process. **56**, Part A, 540-549 (2020).
DOI: https://doi.org/10.1016/j.jmapro.2020.05.012

[14] Ł. Morawiński, C. Jasiński, M. Ciemiorek et al., Solid-state welding of ultrafine grained copper rods. Archiv. Civ. Mech. Eng. **21**, 89 (2021).
DOI: https://doi.org/10.1007/s43452-021-00244-0

[15] M. Ciemiorek, Ł. Morawiński, C. Jasiński et al., Characterization of ultrafine-grained copper joints acquired by rotary friction welding. Archiv. Civ. Mech. Eng. **22**, 9 (2022).
DOI: https://doi.org/10.1007/s43452-021-00326-z

[16] K. Chen, Y. Wu, X. Chen, W. Lei, K. He, J. Chen, H. Liu, Y. Li, Microstructural and mechanical properties of Al–Mg–Si–Cu joint fabricated by rotary friction welding. Journal of Materials Research and Technology **27**, 4204-4212 (2023).
DOI: https://doi.org/10.1016/j.jmrt.2023.10.201

[17] M. Gavalec, I. Barenyi, M. Krbata, M. Kohutiar, S. Balos, M. Pecanac, The Effect of Rotary Friction Welding Conditions on the Microstructure and Mechanical Properties of Ti6Al4V Titanium Alloy Welds. Materials **16** (19), 6492 (2023).
DOI: https://doi.org/10.3390/ma16196492

[18] S. Kunhirunbawon, N. Suwichien, T. Jantarasricha, Friction welding parameter for AA6063 using ANFIS prediction. Int. J. Adv. Manuf. Technol. **128**, 2589-2597 (2023).
DOI: https://doi.org/10.1007/s00170-023-12106-5

[19] H.E. Lakache, A. May, R. Badji, et al., The Impact of the Rotary Friction Welding Pressure on the Mechanical and Microstructural Characteristics of Friction Welds Made of the Alloys TiAl6V4 and 2024 Aluminum. ExpTech. (2023).
DOI: https://doi.org/10.1007/s40799-023-00671-z

[20] A. Rosochowski Severe plastic deformation technology. Dunbeath. Whittles Publishing, (2017).

[21] T.G. Langdon, The impact of bulk nanostructured materials in modern research. Rev. Adv. Mater. Sci. **25**, 11-15 (2010).

[22] V.M. Segal, V.I. Reznikov, A.E. Drobyshevskiy, V.I. Kopylov, Plastic working of metals by simple shear. Russ. Metall. **1**, 99-105 (1981).

[23] M. Lipińska, L. Olejnik, M. Lewandowska, The influence of an ECAP-based deformation process on the microstructure and properties of electrolytic tough pitch copper. Metals (Basel), **53**, 3862-75 (2018).
DOI: https://doi.org/10.1007/s10853-017-1814-y