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MOLTEN-SALT-REACTOR STRUCTURAL MATERIALS DEVLOPMENT

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Abstract - Experimental program Research and development of fluoride salt-cooled nuclear reactor systems aims to contribute to the development of FHR and MSR reactor technology in the area of reactor physics, nuclear - chemical engineering and material research. One of the main objectives of the project is the development of structural material, which includes the verification of experimental production and tests of advanced nickel alloy MoNiCr and subsequent experimental manufacture of selected components from this alloy.

Keywords - Nickel-Based Alloys, Monicr, MSR Structural Materials, Recrystallization.

I. INTRODUCTION

The success of MSR reactors is heavily dependent on the properties of their structural materials during prolonged exposure to high temperatures, and particularly on their compatibility with molten fluoride salts in the reactor’s primary and secondary circuits. The best candidates for operation in LiF-BeF2 and LiF-NaF-KF salts used in generation IV high-temperature nuclear reactors are nickel-based alloys, which contain Cr and Mo and can sustain temperatures up to 750°C. Among them, Inconel 718 and Hastelloy N should be mentioned [1]. The first studies identified nickel-based alloys as those with the highest resistance to corrosion in molten fluoride salts. While, in fact, pure nickel performs best in this respect, it cannot be used because it softens excessively at the reactor’s operating temperature and its creep resistance is negligible [2], [3]. Hastelloy-N, Inconel 718 and related Ni-based alloys are favourable nominee materials for MSR structural materials [4]. The tendency for common alloying elements to form fluorides increases in the following order: W, Mo, Ni, Fe, Cr, Al, Na. Therefore, nickel-based alloys with low Cr and no Al are considered as structural materials for molten salt systems. In fact, from the thermodynamic point of view, any corrosion of elements in nickel-based alloy could be minimal in pure molten fluoride salts because the main components of the salt are more stable than any potential corrosion product [3].

Recrystallization behaviour in MoNiCr alloys has been studied. MoNiCr, a single-phase superalloy, is a nickel-based alloy, added with molybdenum in order to increase its hot oxidation resistance to fluoride salts.

MoNiCr proved deformation strengthening and poor recrystallization performance in the hot forming process [5]. Activating recrystallization is the key to successful severe forming of MoNiCr alloy without producing vast amounts of defects. However, high levels of alloying elements in nickel-based alloys are coupled with high flow stress values. They also complicate the control of microstructural evolution during production at high temperatures, a problem which is encountered in other nickel-based alloys as well. Besides, the requirements for specific properties of nickel-based alloys are usually governed by microstructural evolution during hot deformation, which is closely related to dynamic recrystallization [6]. The presence of different alloying elements in nickel-based superalloys tends to lower the stacking fault energy owing to the formation of widely spaced partial dislocation. Being low-stacking energy materials, the nickel-based superalloys generally exhibit sluggish recovery due to hindered cross slip and climb [7]. The magnitude and, to some extent, the type of deformation controls the recrystallization rate because the amount of stored energy and the number of effective nucleation sites depend on deformation. The type of nucleation site may also be a function of strain. There is a minimum amount of strain, typically 1–3%, below which recrystallization will not occur. Above this strain, the rate of recrystallization increases, levelling out to a maximum value at true strains of ~ 2–4 [8].

II. EXPERIMENT DESCRIPTION

The aim of the experiment is the development and verification of experimental production and tests of advanced nickel-based superalloy MONICR, including melting, casting and forming with the focus on microstructure evolution and subsequent experimental production of selected components and equipment from this alloy. MONICR, a single-phase superalloy, exhibits deformation strengthening and poor recrystallization during hot forming. There is a high tendency to cracking, while recovery and recrystallization processes in the superalloy structure are retarded by alloying elements.

Nevertheless, it is crucial to transform coarse primary grains in casting structure into an equiaxed-recrystallized structure appropriate for forming. Being low stacking energy materials, as the presence of different alloying elements in nickel based superalloys tends to lower it, the nickel based superalloys generally exhibit sluggish recovery due to hindered cross slip and climb [9]. The high concentration of alloying elements leads to high deformation resistance as well as the difficulties of controlling microstructure in the hot working process, similar to many other nickel-based alloys [6], [10].

III. MELTING AND CASTING OF NICKEL-BASED SUPERALLOY

At the first stage of this experiment, the main purpose was melting and casting of material for further testing. The MONICR alloy was cast in the new ceramic crucible with a lining made up mainly from Al2O3 in vacuum induction furnace in COMTES FHT. The batch consisted of several very clean elements as an example nickel briquettes that contained more than 99.8 wt. % Ni. The total amount was 60 kg. The technique of argon was used during the melting process. The bubbles of gas were going through melt and helped to flow the impurities out. In addition, the level of vacuum was very low – 200Pa. The power input of furnace was approximately 100 kW at the start of melting process and afterwards 40 kW for holding on the temperature. After final alloying, the melt was deoxidized by NiMg15 alloy (1kg/ton). The melt was subsequently poured at temperature 1600 °C into ingot mould with circle cross-section. The pouring cup was provided with electrical resistance heating which facilitated smooth pouring and prevented the metal from freezing in the sprue. The exothermic lining and powder were applied to the upper part of the ingot to solidification carry out here up to the end. The final ingots appearance are captured in Fig. 1 and Fig. 2.

Fig. 1 Final appearance of the solid ingot.

Fig. 2 Raw cast of MoNiCr alloy plate.

The chemical composition was carried out on the optical emission spectrometer BRUKER Q4 TASMAN. The chemical composition of the experimental alloy is given in Table. I.

Alloy	Mo	Cr	Ti	Fe	Mn	Nb	Al	W	Ni
MONICR	15.2	5.9	0.001	1.01	0.04	0.02	0.005	0.007	bal

TABLE I. Chemical composition of experimental alloy.

Macroscopic defects were not observed in the bottom part of the ingot from the macrostructure point of view (Fig. 3). The thin casting crust was made of fine equiaxed crystals with random orientation due to rapid cooling from the cast-iron wall. This structure was followed by an area of coarse columnar grains whose orientation was in the direction of heat dissipation.

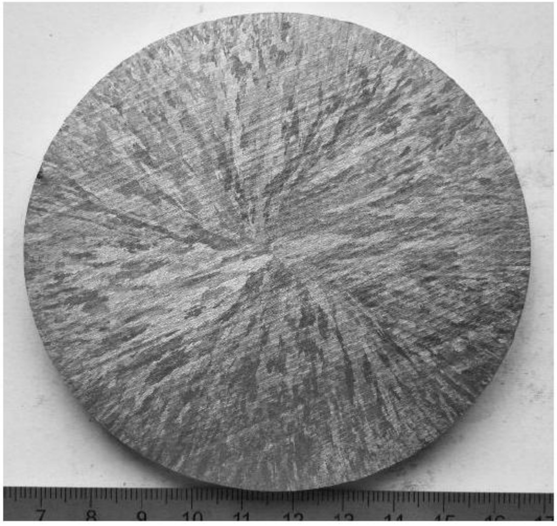

Fig. 3 Macrostructure of the ingot.

The cast state microstructure was induced by etching in Glyceregia reagent. Structure documentation was performed on a NIKON EPIPHOT 200 optical microscope. The common feature of the cast ingot was a coarse casting microstructure with a noticeable dendritic segregation. See Fig. 4.

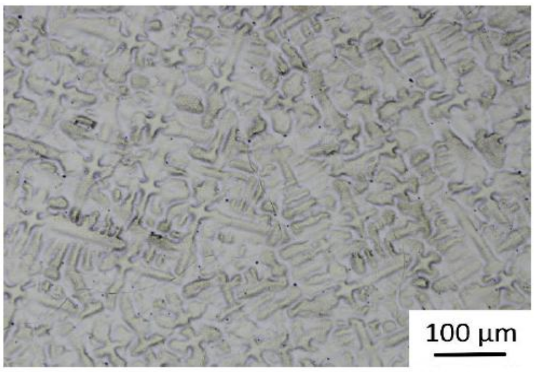

Fig. 4 Dendritic segregation of the as – cast state.

IV. RECRYSTALLIZATION BEHAVIOUR

Nickel-based superalloys are difficult to recrystallize. Even after hot forming, their microstructure tends to be non-uniform and contains coarse and fine grains [11]. It is therefore important to determine the lowest amount of deformation, which still ensures complete recrystallization and provides as uniform recrystallized grains as possible. Microstructures obtained in the temperature interval of 750 – 1150°C are illustrated in Fig. 5 – Fig. 8. In the MoNiCr alloy, elements remain in the solid solution. Foreign atoms in the base metal lattice retard its static recrystallization. This means that at the same temperature, the process takes longer to complete, and during continuous heating, recrystallization starts later in a metal with impurities [12]. As these micrographs show, lower recrystallization annealing temperatures led to only partial recrystallization. Recrystallized grains formed along boundaries of deformed prior grains. At 1050°C, the recrystallized grains were of non-uniform size. Only the temperature of 1150°C produced equiaxed-recrystallized grains and led to complete recrystallization of the MoNiCr alloy. Fig. 9 and Table I list hardness readings. They clearly indicate the decrease in hardness with increasing annealing temperature.

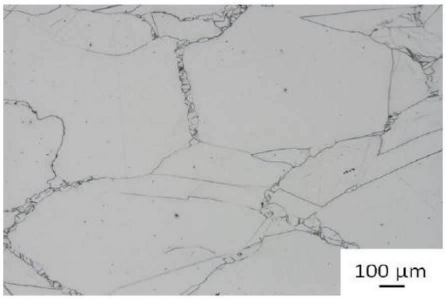

Fig. 5 As-rolled condition.

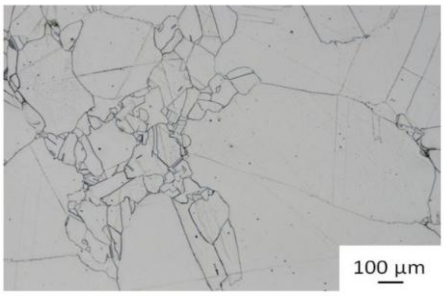

Fig. 6 Annealing at 750°C.

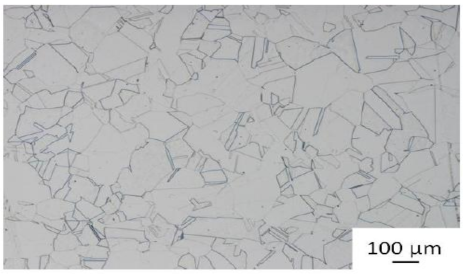

Fig. 7 Annealing at 1050°C.

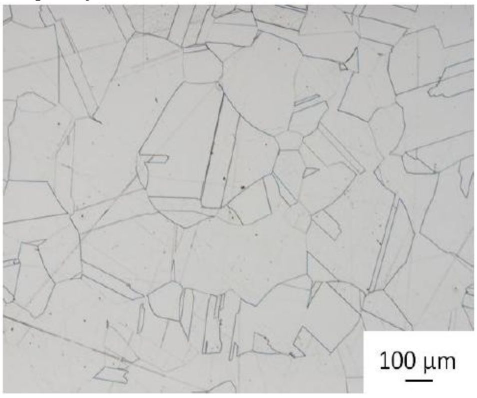

Fig. 8 Annealing at 1150 °C.

Specimen	Temperature	HV10
1	20	290
2	750	234
3	850	216
4	950	164
5	1050	162
6	1150	151

Table I. Hardness values HV10 – recrystallization annealing.

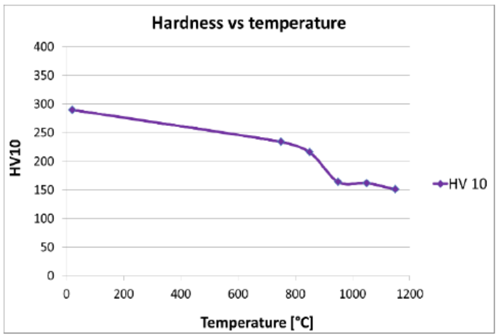

Fig. 9 Dependence of MoNiCr hardness on annealing temperature.

V. EXPERIMENTAL MANUFACTURE OF SELECTED COMPONENTS

The material in the form for the production of flange joints, drawn wires (Fig. 10) and rolled sheets (Fig. 11) for experimental welding were produced within the scope of the project. The production of welding wires was performed by cutting out 10 mm diameter rods on the EDM machine, followed by forming on swaging machine to Ø2.36 mm. The final dimension of Ø1.94 mm, the length of a single wire of about 110 cm was already achieved by drawing the wires.

Maximum reduction during cold forging was up to 36%, followed by annealing at 1150 °C for 90min, then cooled to water to prevent precipitation of intermetallic phases. The average hardness value after annealing was about 150 HV10. The final welding wire Ø1.94 mm had a final average hardness of 335 HV10 after drawing.

Fig. 10 Wires for welding.

Fig. 11 Rolled sheets.

VI. CONCLUSION

Development and verification of experimental production of advanced nickel-based superalloy MONICR were the main objectives of the research. Extensive work has been devoted to activating recrystallization in as-cast MoNiCr alloy, the key to severe forming of this alloy without producing vast amounts of defects. The research aims to contribute to the development of Fluoride-Salt-Cooled High-Temperature Reactors and Molten-Salt-Reactor technology in the area of reactor physics, nuclear - chemical engineering and material research.

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REFERENCES

[1] P. Hosnedl, J.Dlouhy, “Compatibility of construction materials for high temperature reactors and fluoride salt melt technology”. Research report. COMTES FHT. 2010.

[2] P. Slama, M. Marecek, “Corrosion testing of nickel alloy for molten salt reactors”. Journal of Achievements in Materials and Manufacturing Eng. 2015, 70(2). Gliwice, Poland; pp. 8/78-85, ISSN 1734-8412.

[3] X. Ye, H. Ai, Z. Guo, H. Huang, L. Jiang, J. Wang, Z. Li, X. Zhou, “The high-temperature corrosion of Hastelloy N alloy (UNS N10003) in molten fluoride salts analysed by STXM, XAS, XRD, SEM, EPMA, TEM/EDS”. Corrosion Science 2016, 106, pp. 249–259.

[4] F. Ouyang, Ch. Chang, J. Kai, “Long-term corrosion behaviors of Hastelloy-N and Hastelloy-B3 in moisture-containing molten FLiNaK salt environments”. Journal of Nuclear Materials 2014, 446, pp. 81–89.

[5] M. Koukolikova, P. Slama, Z. Novy, P. Svoboda, P. Toman, M. Marecek, J. Uhlir, “Research of materials and components for molten salt reactors”. Proceedings of the ANS Annual Meeting. Transactions of the American Nuclear Society, Vol. 116, 2017, San Francisco, California, USA, June 11–15, 2017; pp. 523-526, ISSN 0003-018X.

[6] Y. Wu, M. Zhang, X. Xie, F. Lin, S. Zhao, “Dynamic recrystallization of a new nickel-based alloy for 700°C A-USC power plant applications with different initial states: as-homogenized and as-forged”. Materials Science & Engineering 2016, 662, p283-295.

[7] S. Kumar, T. Raghu, P.P. Bhattacharjee, G. Appa Rao, U. Borah, “Strain rate dependent microstructural evolution during hot deformation of a hot isostatically processed nickel base superalloy”. Journal of Alloys and Compounds 2016, 681, pp. 28-42.

[8] F.J. Humphreys, M. Hatherly, “Recrystallization of single-phase alloys. In Recrystallization and Related Annealing Phenomena”. 2nd ed.; Sleeman D.; Elsevier Ltd.: Oxford, UK, 2004; pp. 215-266. ISBN 0 – 08 - 044164 5.

[9] S. Kumar et al.: “Strain rate dependent microstructural evolution during hot deformation of a hot isostatically processed nickel base superalloy,” Journal of Alloys and Compounds, 681, 28-42 (2016).

[10] P. Podany, J. Dlouhy, Z. Novy, “Recrystallization Behaviour of Nickel-Based Superalloy”, Materiali in Tehnologije, Vol. 50, (2), pp. 199-205, (2016).

[11] P. Podany, M. Koukolikova, P. Motycka, P. Slama, “Recrystallization Behaviour of Nickel-Based Superalloys for Molten Salt Reactors”. In: Transactions of the American Nuclear Society. Jun 17, 2018, Philadelphia, Pennsylvania, USA, USA. [online]. Illinois, 2018. p. 3 / 1445-1447. ISSN 0003-018X.

[12] R. Choteborsky, “Material science”, 1st ed.; Czech university of life sciences, Prague 2006; pp. 30-32, ISBN 80–213–1442–7.

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